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Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector

*Industrial Emissions Directive 2010/75/EU
(Integrated Pollution Prevention and Control)*

Thomas Brinkmann, Germán Giner Santonja,
Hande Yükseler, Serge Roudier,
Luis Delgado Sancho

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Authors:

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Title Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector

Abstract
The BAT reference document (BREF) entitled 'Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector' forms part of a series presenting the results of an exchange of information between EU Member States, the industries concerned, non-governmental organisations promoting environmental protection, and the Commission, to draw up, review and, where necessary, update BAT reference documents as required by Article 13(1) of the Directive 2010/75/EU on industrial emissions. This document is published by the European Commission pursuant to Article 13(6) of the Directive. This BREF for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector concerns the activities specified in Sections 4 and 6.11 of Annex I to Directive 2010/75/EU, namely:

- Section 4: Chemical industry;
- Section 6.11: Independently operated treatment of waste water not covered by Council Directive 91/271/EEC and discharged by an installation undertaking activities covered under Section 4 of Annex I to Directive 2010/75/EU.

This document also covers the combined treatment of waste water from different origins if the main pollutant load originates from the activities covered under Section 4 of Annex I to Directive 2010/75/EU.

In particular, this document covers the following issues:
- environmental management systems;
- water saving;
- waste water management, collection, and treatment;
- waste management;
- treatment of waste water sludge with the exception of incineration;
- waste gas management, collection, and treatment;
- flaring;
- diffuse emissions of volatile organic compounds (VOCs) to air;
- odour emissions;
- noise emissions.

Important issues for the implementation of Directive 2010/75/EU in the chemical industry are emissions to air and water. This BREF contains six chapters. Chapter 1 provides general information on waste water and waste gas. Chapter 2 provides data and information concerning the environmental performance of waste water treatment plants (WWTPs) at chemical sites. Chapter 3 describes in more detail the techniques to prevent or, where this is not practicable, to reduce the environmental impact of operating installations in this sector that were considered in determining the BAT. This information includes, where relevant, the environmental performance levels (e.g. emission and consumption levels) which can be achieved by using the techniques, the associated monitoring and the costs and the cross-media issues associated with the techniques. Chapter 4 presents the BAT conclusions as defined in Article 3(12) of the Directive. Chapter 5 presents information on 'emerging techniques' as defined in Article 3(14) of the Directive. Chapter 6 is dedicated to concluding remarks and recommendations for future work.

Acknowledgements

This document is one from the series of documents listed below (at the time of writing, the following documents have been drafted):

Reference Document on Best Available Techniques	Code
Ceramic Manufacturing Industry	CER
Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector	*CWW*
Emissions from Storage	EFS
Energy Efficiency	ENE
Ferrous Metals Processing Industry	FMP
Food, Drink and Milk Industries	FDM
Industrial Cooling Systems	ICS
Intensive Rearing of Poultry and Pigs	IRPP
Iron and Steel Production	IS
Large Combustion Plants	LCP
Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers	LVIC-AAF
Large Volume Inorganic Chemicals – Solids and Others Industry	LVIC-S
Large Volume Organic Chemical Industry	LVOC
Management of Tailings and Waste-rock in Mining Activities	MTWR
Manufacture of Glass	GLS
Manufacture of Organic Fine Chemicals	OFC
Non-ferrous Metals Industries	NFM
Production of Cement, Lime and Magnesium Oxide	CLM
Production of Chlor-alkali	CAK
Production of Polymers	POL
Production of Pulp, Paper and Board	PP
Production of Speciality Inorganic Chemicals	SIC
Production of Wood-based Panels	WBP
Refining of Mineral Oil and Gas	REF
Slaughterhouses and Animals By-products Industries	SA
Smitheries and Foundries Industry	SF
Surface Treatment of Metals and Plastics	STM
Surface Treatment Using Organic Solvents	STS
Tanning of Hides and Skins	TAN
Textiles Industry	TXT
Waste Incineration	WI
Waste Treatment	WT
Reference Document	
Economics and Cross-media Effects	ECM
Monitoring of Emissions to Air and Water from IED installations	ROM

Electronic versions of draft and finalised documents are publicly available and can be downloaded from http://eippcb.jrc.ec.europa.eu/.

PREFACE

1. Status of this document

Unless otherwise stated, references to 'the Directive' in this document refer to Directive 2010/75/EU of the European Parliament and the Council on industrial emissions (integrated pollution prevention and control) (Recast).

The original best available techniques (BAT) reference document (BREF) for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector was adopted by the European Commission in 2003. This document is the result of a review of that BREF. The review commenced in January 2008.

This BAT reference document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector forms part of a series presenting the results of an exchange of information between EU Member States, the industries concerned, non-governmental organisations promoting environmental protection and the Commission, to draw up, review and, where necessary, update BAT reference documents as required by Article 13(1) of the Directive. This document is published by the European Commission pursuant to Article 13(6) of the Directive.

As set out in Article 13(5) of the Directive, the Commission Implementing Decision (EU) 2016/902 on the BAT conclusions contained in Chapter 4 was adopted on 30 May 2016 and published on 9 June 2016[1].

2. Participants in the information exchange

As required in Article 13(3) of the Directive, the Commission has established a forum to promote the exchange of information, which is composed of representatives from Member States, the industries concerned and non-governmental organisations promoting environmental protection (Commission Decision of 16 May 2011 establishing a forum for the exchange of information pursuant to Article 13 of the Directive 2010/75/EU on industrial emissions (2011/C 146/03), OJ C 146, 17.05.2011, p. 3).

Forum members have nominated technical experts constituting the technical working group (TWG) that was the main source of information for drafting this document. The work of the TWG was led by the European IPPC Bureau (of the Commission's Joint Research Centre).

3.Structure and contents of this document

Chapter 1 provides general information on waste water and waste gas, including general information on management and treatment systems used within the chemical industry.

Chapter 2 provides data and information concerning the environmental performance of waste water treatment plants (WWTPs) at chemical sites, and in operation at the time of writing, in terms of current emissions, consumption and nature of raw materials, water consumption, use of energy and the generation of waste.

Chapter 3 describes in more detail the techniques to prevent or, where this is not practicable, to reduce the environmental impact of operating installations in this sector that were considered in determining the BAT. This information includes, where relevant, the environmental performance levels (e.g. emission and consumption levels) which can be achieved by using the

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[1] OJ L 152, 9.6.2016, p. 23.

techniques, the associated monitoring and the costs and the cross-media issues associated with the techniques.

Chapter 4 presents the BAT conclusions as defined in Article 3(12) of the Directive.

Chapter 5 presents information on 'emerging techniques' as defined in Article 3(14) of the Directive.

Concluding remarks and recommendations for future work are presented in Chapter 6.

4.Information sources

This document is based on information collected from a number of sources, in particular through the TWG that was established specifically for the exchange of information under Article 13 of the Directive. The information has been collated and assessed by the European IPPC Bureau (of the Commission's Joint Research Centre) who led the work on determining BAT, guided by the principles of technical expertise, transparency and neutrality. The work of the TWG and all other contributors is gratefully acknowledged.

The BAT conclusions have been established 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 these key issues;
- identification of the best environmental performance levels, on the basis of the available data in the European Union and worldwide;
- examination of the conditions under which these environmental performance levels were achieved, such as costs, cross-media effects, and the main driving forces involved in the implementation of the techniques;
- selection of the best available techniques (BAT), their associated emission levels (and other environmental performance levels) and the associated monitoring for this sector according to Article 3(10) of, and Annex III to, the Directive.

Expert judgement by the European IPPC Bureau and the TWG has played a key role in each of these steps and the way in which the information is presented here.

Where available, economic data have been given together with the descriptions of the techniques presented in Chapter 3. These data give a rough indication of the magnitude of the costs and benefits. However, the actual costs and benefits of applying a technique may depend strongly on the specific situation of the installation concerned, which cannot be evaluated fully in this document. In the absence of data concerning costs, conclusions on the economic viability of techniques are drawn from observations on existing installations.

5.   Review of BAT reference documents (BREFs)

BAT is a dynamic concept and so the review of BREFs is a continuing process. For example, new measures and techniques may emerge, science and technologies are continuously developing and new or emerging processes are being successfully introduced into the industries. In order to reflect such changes and their consequences for BAT, this document will be periodically reviewed and, if necessary, updated accordingly.

6.   Contact information

All comments and suggestions should be made to the European IPPC Bureau at the Directorate B - Growth and Innovation at the following address:

European Commission
JRC Directorate B - Growth and Innovation
European IPPC Bureau
Edificio Expo
c/Inca Garcilaso, 3
E-41092 Seville, Spain
Telephone: +34 95 4488 284
Fax: +34 95 4488 426
E-mail: JRC-IPTS-EIPPCB@ec.europa.eu
Internet: http://eippcb.jrc.ec.europa.eu

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

4   BEST AVAILABLE TECHNIQUES (BAT) CONCLUSIONS FOR COMMON WASTE WATER/WASTE GAS TREATMENT/MANAGEMENT SYSTEMS IN THE CHEMICAL SECTOR

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SCOPE

This BREF for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector concerns the activities specified in Sections 4 and 6.11 of Annex I to Directive 2010/75/EU, namely:

- Section 4: Chemical industry;
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This document also covers the combined treatment of waste water from different origins if the main pollutant load originates from the activities covered under Section 4 of Annex I to Directive 2010/75/EU.

In particular, this document covers the following issues:

- environmental management systems;
- water saving;
- waste water management, collection, and treatment;
- waste management;
- treatment of waste water sludge with the exception of incineration;
- waste gas management, collection, and treatment;
- flaring;
- diffuse emissions of volatile organic compounds (VOCs) to air;
- odour emissions;
- noise emissions.

Other reference documents which could be relevant for the activities covered by this document are the following:

- Production of Chlor-alkali (CAK);
- Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers (LVIC-AAF);
- Manufacture of Large Volume Inorganic Chemicals – Solids and Others Industry (LVIC-S);
- Production of Speciality Inorganic Chemicals (SIC);
- Large Volume Organic Chemical Industry (LVOC);
- Manufacture of Organic Fine Chemicals (OFC);
- Production of Polymers (POL);
- Emissions from Storage (EFS);
- Energy Efficiency (ENE);
- Monitoring of Emissions to Air and Water from IED installations (ROM);
- Industrial Cooling Systems (ICS);
- Large Combustion Plants (LCP);
- Waste Incineration (WI);
- Waste Treatments Industries (WT);
- Economics and Cross-media Effects (ECM).

The scope of this document does not include matters that only concern safety in the workplace or the safety of products because these matters are not covered by the Directive. They are discussed only where they affect matters within the scope of the Directive.

BREF interface

A schematic on the main and typical interface between the CWW BREF and the other chemical BREFs concerning waste water treatment techniques is shown in Figure 1.
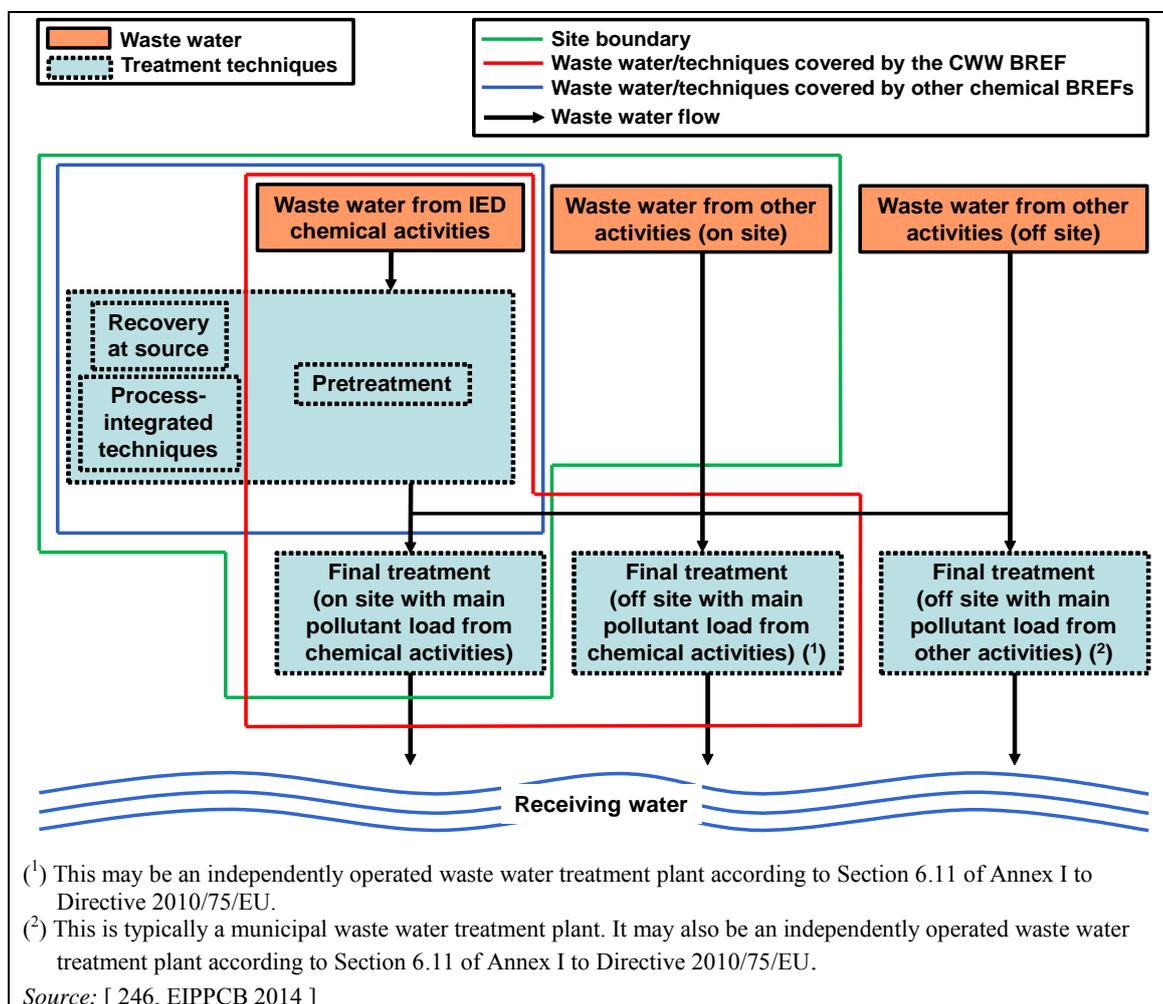
Figure 1: **The main and typical interface between the CWW BREF and the other chemical BREFs concerning waste water treatment techniques**

1   GENERAL INFORMATION

1.1   The chemical industry sector in Europe

1.1.1   Industrial and economic development

The EU chemical industry sector provides a significant contribution to the EU economy. It is one of its most international and competitive industries, connected to a wide field of processing and manufacturing activities. Its output covers a wide range of chemical products, and supplies virtually all sectors of the economy. In 2011, total chemical sales in the EU-27 amounted to EUR 539 billion, 19.6 % of world chemical sales in value terms. This share had declined from 29.8 % in 2001 although the total value of sales had been growing continuously, but overall world chemical sales were growing at an even faster pace. In 2011, the EU-27 was the leading exporter and importer of chemicals in the world, accounting for nearly 40 % of global trade, defined as the total value of exports plus imports including intra-EU trade [2, CEFIC 2012].

The chemical sector in the EU-27 employed a total staff of about 1.19 million in 2011. The sector also generated additional indirect jobs via the value chain, which was two times higher than through direct employment. Direct employment decreased by an average annual rate of 1.9 % from 2002 to 2011 [2, CEFIC 2012].

1.1.2   Geographic distribution

Eight EU Member States accounted for approximately 90 % of European chemical production in 2011 (Figure 1.1). Germany remained the largest chemicals producer in Europe, followed by France, the Netherlands, and Italy. Together, these four countries generated 64.4 % of EU-27 chemical sales, valued at EUR 347.2 billion. The share was equivalent to nearly 90 %, or EUR 480.3 billion, when the United Kingdom, Spain, Belgium, and Poland were included. The other 19 EU Member States generated approximately 10 % of EU-27 chemical sales, valued at EUR 58.8 billion, approximately half of which was attributable to four EU Member States, namely Sweden, Austria, the Czech Republic and Finland [2, CEFIC 2012].
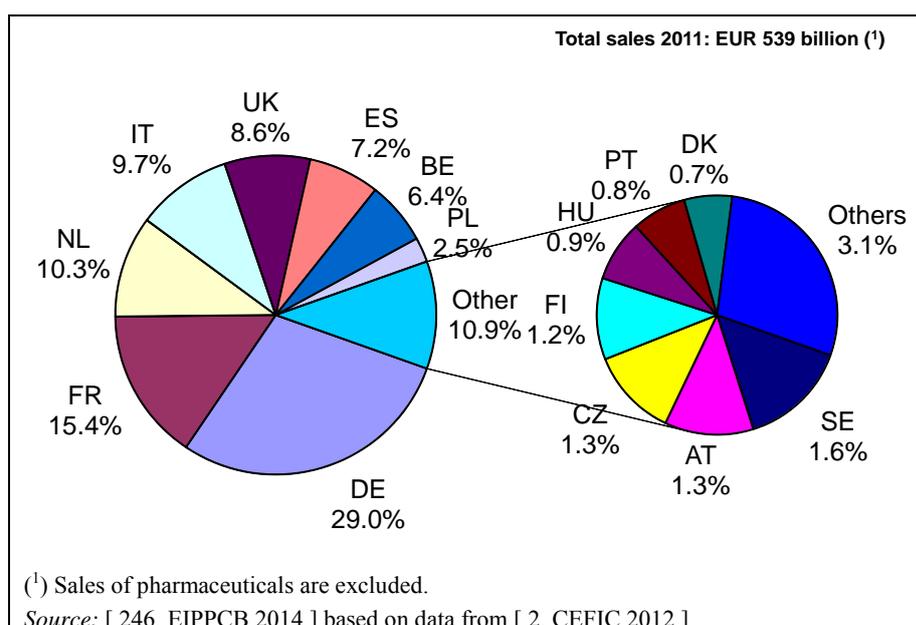
Figure 1.1:   Share per EU-27 Member State of total chemical industry sales in 2011

1.1.3 Integrated chemical sites in Europe

A large share of chemical production in the EU-27 is carried out on integrated chemical sites which present both challenges and opportunities with respect to pollution prevention and control. Challenges include dealing with the possible complexity of the interconnections and interdependence between chemical installations. Opportunities include the recycling or reuse of material, energy or water as well as the use of common equipment that can enhance the capability and efficiency to respond to emergency situations and to prevent or minimise environmental impacts and damage. Central waste water treatment plants and central incineration/oxidation plants are examples of such common equipment. In accordance with the principles of the Industrial Emissions Directive (2010/75/EU) and other Community legislation, prevention of pollution is preferred over control, when this is feasible. This is the reason why the treatment of waste water or waste gas is an option that is considered after examining the various options to prevent emissions and waste.

Incineration can also provide a means for the recovery of energy (e.g. the production of steam and/or electricity) and materials (often chemicals) from wastes. When central incineration is carried out, special attention is usually given to periods when the central treatment is unavailable, e.g. for maintenance reasons. In such cases, backup systems (e.g. decentralised) are generally available.

1.2   Environmental relevance of the chemical industry

1.2.1   Overview

Issues of environmental relevance of the chemical industry sector include [15, CEFIC 2012]:

*   energy efficiency;
*   emissions of (halogenated) organic compounds, nutrients (nitrogen, phosphorus) and metals to water;
*   emissions of volatile organic compounds (VOCs) and acidifying gases (ammonia, sulphur oxides and nitrogen oxides) to air;
*   waste generation.

Much of the data in the following sections was taken from the European Pollutant Release and Transfer Register (E-PRTR) that covers large industrial installations. For the year 2010, the E-PRTR contained emission data from approximately 14 000 installations in the EU-27 plus Iceland, Liechtenstein, Norway and Serbia, of which approximately 900 belonged to the chemical industry sector. The definition of the chemical industry sector in the E-PRTR is the same as in the Industrial Emissions Directive 2010/75/EU (IED) [5, Directive 2010/75/EU 2010] [16, E-PRTR 2013].

The data from the E-PRTR give an overview of the relative importance of a specific pollutant for a given industry sector. However, total emissions from a particular industry sector are usually higher because the E-PRTR only contains emission data from those installations exceeding a certain threshold value. Moreover, emissions to water may occur indirectly via municipal or independently operated industrial waste water plants. In these cases emissions would be reported under another category.

Other data were taken from the statistical database of Eurostat. The sectors/activities are defined in the Statistical Classification of Economic Activities in the European Community (NACE) [23, Eurostat 2013].

1.2.2   Energy efficiency

The total consumption of energy of the chemical industry sector amounted to 50.4 million tonnes of oil equivalent (TOE) in 2009 (equivalent to 2.1 EJ). From 1990 to 2009, consumption fell by nearly 27 %. During this period, annual production climbed on average 2.5 % while energy consumption fell 1.7 % which is equivalent to an overall decrease in energy intensity of approximately 55 % [15, CEFIC 2012]. In 2011, the total final energy consumption in the EU-27 amounted to 46.19 EJ ($1 \, EJ = 10^{18}$ J) (Figure 1.2). The largest share of energy was consumed for transport, followed by industrial activities and residential consumption. The chemical and petrochemical industry sector consumed 2.33 EJ which was equivalent to 5.0 % of the total final energy consumed in the EU-27.

Figure 1.2 caption data (labels within figure):

- Services: 5.88 EJ, 12.7 %
- Other sectors/activities: 1.63 EJ, 3.5 %
- Total final energy consumption: 46.19 EJ (¹)
- Paper, pulp and print: 1.38 EJ, 3.0 %
- Food and tobacco: 1.17 EJ, 2.5 %
- Residential: 11.42 EJ, 24.7 %
- Non-metallic minerals: 1.56 EJ, 3.4 %
- Transport: 15.24 EJ, 33.0 %
- Industry: 12.02 EJ, 26.0 %
- Chemical and petrochemical: 2.33 EJ, 5.0 %
- Metals: 2.59 EJ, 5.6 %
- Other industry: 2.99 EJ, 6.5 %

(¹) Coverage: EU-27; sectors/activities as defined in the Statistical Classification of Economic Activities in the European Community (NACE); 'Chemical and petrochemical' refers to NACE C19 – C22.

Source: [246, EIPPCB 2014] based on data from [23, Eurostat 2013]

Figure 1.2:   **Total final energy consumption by industry sector/activity in the EU-27 in 2011**

1.2.3   Emissions to water

1.2.3.1   Organic compounds

Emissions of organic compounds to water by industry sector, reported as total organic carbon (TOC), are shown in Figure 1.3. In 2010, 126 installations of the chemical industry sector emitted a total of 29.5 kt of TOC to water, representing 4.0 % of the total amount of TOC emitted to water by all installations covered by the E-PRTR. The largest share of TOC emissions originated from urban waste water treatment plants, followed by intensive aquaculture, and then by paper and wood production and processing. Within the chemical industry sector, the production of basic organic chemicals was responsible for more than 65 % of all TOC emissions.

Independently operated industrial waste water treatment plants:
19 installations, 16.8 kt, 2.3 %

Other waste and waste water management:
52 installations, 17.7 kt, 2.4 %

Total number of installations: 1921 ([1])
Total TOC emissions to water: 746.5 kt

Urban waste water treatment:
790 installations, 293.0 kt, 39.2 %

Food and beverages:
47 installations, 17.5 kt, 2.3 %

Other sectors/activities:
108 installations, 20.9 kt, 2.8 %

Basic inorganic chemicals:
15 installations, 6.4 kt, 0.9 %

Basic pharmaceutical products:
19 installations, 2.6 kt, 0.3 %

Other chemicals:
5 installations, 0.7 kt, 0.1 %

Paper and wood:
195 installations, 152.2 kt, 20.4 %

Chemical industry:
126 installations, 29.5 kt, 4.0 %

Intensive aquaculture:
584 installations, 198.9 kt, 26.6 %

Basic organic chemicals:
87 installations, 19.8 kt, 2.7 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of total organic carbon (TOC) (as total C or COD/3) of more than 50 t/yr; normal operation.
NB: COD = chemical oxygen demand.
Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.3:   Emissions of organic compounds to water by industry sector/activity in Europe in 2010

1.2.3.2 Halogenated organic compounds

Emissions of halogenated organic compounds to water by industry sector, reported as adsorbable organically bound halogens (AOX), are shown in Figure 1.4. In 2010, 33 installations of the chemical industry sector emitted a total of 353 t of AOX to water, representing 8.5 % of the total amount of AOX emitted to water by all installations covered by the E-PRTR. The largest share of AOX emissions originated from paper and wood production and processing, followed by urban waste water treatment plants. Within the chemical industry sector, the production of basic organic chemicals was responsible for almost 90 % of all AOX emissions.

Other waste and waste water management:
22 installations, 591 t, 14.2 %

Total number of installations: 374 ([1])
Total AOX emissions to water: 4166 t

Urban waste water treatment:
232 installations, 1045 t, 25.1 %

Other sectors/activities:
26 installations, 179 t, 4.3 %

Basic inorganic chemicals:
6 installations, 25 t, 0.6 %

Chemical industry:
33 installations, 353 t, 8.5 %

Other chemicals:
6 installations, 14 t, 0.3 %

Paper and wood:
61 installations, 1997 t, 47.9 %

Basic organic chemicals:
21 installations, 314 t, 7.5 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of adsorbable organically bound halogens (AOX) of more than 1 t/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.4:   Emissions of halogenated organic compounds to water by industry sector/activity in Europe in 2010

1.2.3.3   Nitrogen

Emissions of nitrogen to water by industry sector are shown in Figure 1.5. In 2010, 93 installations of the chemical industry sector emitted a total of 26.0 kt of total nitrogen to water, representing 5.9 % of the total amount of nitrogen emitted to water by all installations covered by the E-PRTR. The largest share of nitrogen emissions originated from urban waste water treatment plants. Within the chemical industry sector, the production of basic organic chemicals, the production of basic inorganic chemicals, and the production of fertilisers were responsible for more than 90 % of all nitrogen emissions.

Other waste and waste water management:
67 installations, 12.9 kt, 2.9 %

Intensive aquaculture:
377 installations, 37.7 kt, 8.6 %

Metals:
36 installations, 8.6 kt, 2.0 %

Paper and wood:
55 installations, 6.4 kt, 1.5 %

Other sectors/activities:
70 installations, 13.1 kt, 3.0 %

Total number of installations: 1542 ([1])
Total nitrogen emissions to water: 438.6 kt

Fertilisers:
18 installations, 7.4 kt, 1.7 %

Basic pharmaceutical products:
7 installations, 1.7 kt, 0.4 %

Other chemicals:
3 installations, 0.2 kt, 0.0 %

Basic organic chemicals:
29 installations, 8.1 kt, 1.9 %

Chemical industry:
93 installations, 26.0 kt, 5.9 %

Basic inorganic chemicals:
36 installations, 8.5 kt, 1.9 %

Urban waste water treatment:
844 installations, 334.0 kt, 76.1 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of total nitrogen of more than 50 t/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.5:   Emissions of total nitrogen to water by industry sector/activity in Europe in 2010

1.2.3.4   Phosphorus

Emissions of phosphorus to water by industry sector are shown in Figure 1.6. In 2010, 55 installations of the chemical industry sector emitted a total of 10.3 kt of total phosphorus to water, representing 17.5 % of the total amount of phosphorus emitted to water by all installations covered by the E-PRTR. The largest share of phosphorus emissions originated from urban waste water treatment plants. Within the chemical industry sector, a few installations producing basic pharmaceutical products were responsible for more than 90 % of all phosphorus emissions.

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of total phosphorus of more than 5 t/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]
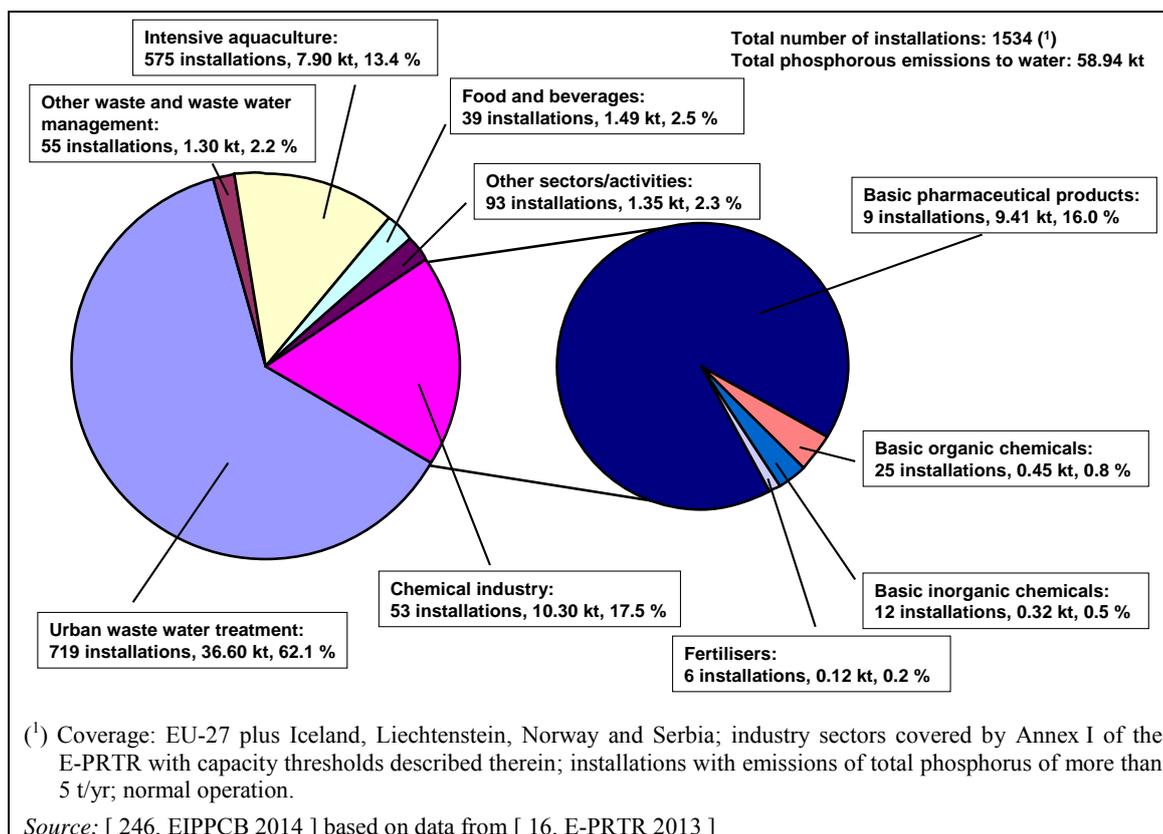
Figure 1.6:   Emissions of total phosphorus to water by industry sector/activity in Europe in 2010

1.2.3.5   Cadmium

Emissions of cadmium to water by industry sector are shown in Figure 1.7. In 2010, 25 installations of the chemical industry sector emitted a total of 0.89 t of cadmium to water, representing 4.8 % of the total amount of cadmium emitted to water by all installations covered by the E-PRTR. The largest share of cadmium emissions originated from urban waste water treatment plants. Within the chemical industry sector, the production of basic inorganic chemicals was responsible for almost 70 % of all cadmium emissions.

Non-ferrous metals:
21 installations, 1.25 t, 6.8 %

Underground mining:
10 installations, 0.75 t, 4.1 %

Total number of installations: 367 ([1])
Total cadmium emissions to water: 18.53 t

Iron and steel:
13 installations, 1.27 t, 6.9 %

Energy:
43 installations, 1.01 t, 5.4 %

Paper and wood:
48 installations, 1.00 t, 5.4 %

Basic inorganic chemicals:
16 installations, 0.62 t, 3.4 %

Other sectors/activities:
52 installations, 1.14 t, 6.1 %

Urban waste water treatment:
155 installations, 11.21 t, 60.5 %

Chemical industry:
25 installations, 0.89 t, 4.8 %

Other chemicals:
2 installations, 0.01 t, 0.1 %

Basic organic chemicals:
7 installations, 0.26 t, 1.4 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of cadmium and compounds (as Cd) of more than 5 kg/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.7:   Emissions of cadmium to water by industry sector/activity in Europe in 2010

1.2.3.6   Chromium

Emissions of chromium to water by industry sector are shown in Figure 1.8. In 2010, 44 installations of the chemical industry sector emitted a total of 63.8 t of chromium to water, representing 22.4 % of the total amount of chromium emitted to water by all installations covered by the E-PRTR. The largest share of chromium emissions originated from urban waste water treatment plants. Within the chemical industry sector, the production of basic inorganic chemicals was responsible for 65 % of all chromium emissions.

Surface treatment using organic solvents:
2 installations, 15.3 t, 5.4 %

Thermal power station/Combustion:
31 installations, 30.5 t, 10.7 %

Iron and steel:
22 installations, 14.5 t, 5.1 %

Total number of installations: 429 ([1])
Total chromium emissions to water: 284.4 t

Other sectors/activities:
135 installations, 30.1 t, 10.6 %

Basic inorganic chemicals:
17 installations, 41.9 t, 14.7 %

Tanning of hides and skins:
2 installations, 31.6 t, 11.1 %

Chemical industry:
44 installations, 63.8 t, 22.4 %

Other chemicals:
2 installations, 0.5 t, 0.2 %

Urban waste water treatment:
193 installations, 98.6 t, 34.6 %

Basic organic chemicals:
25 installations, 21.4 t, 7.5 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of chromium and compounds (as Cr) of more than 50 kg/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.8:   Emissions of chromium to water by industry sector/activity in Europe in 2010

1.2.3.7   Copper

Emissions of copper to water by industry sector are shown in Figure 1.9. In 2010, 58 installations of the chemical industry sector emitted a total of 17.0 t of copper to water, representing 2.9 % of the total amount of copper emitted to water by all installations covered by the E-PRTR. The largest share of copper emissions originated from urban waste water treatment plants followed by opencast mining and quarrying. Within the chemical industry sector, the production of basic organic chemicals was responsible for 65 % of all copper emissions.

(¹) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of copper and compounds (as Cu) of more than 50 kg/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]
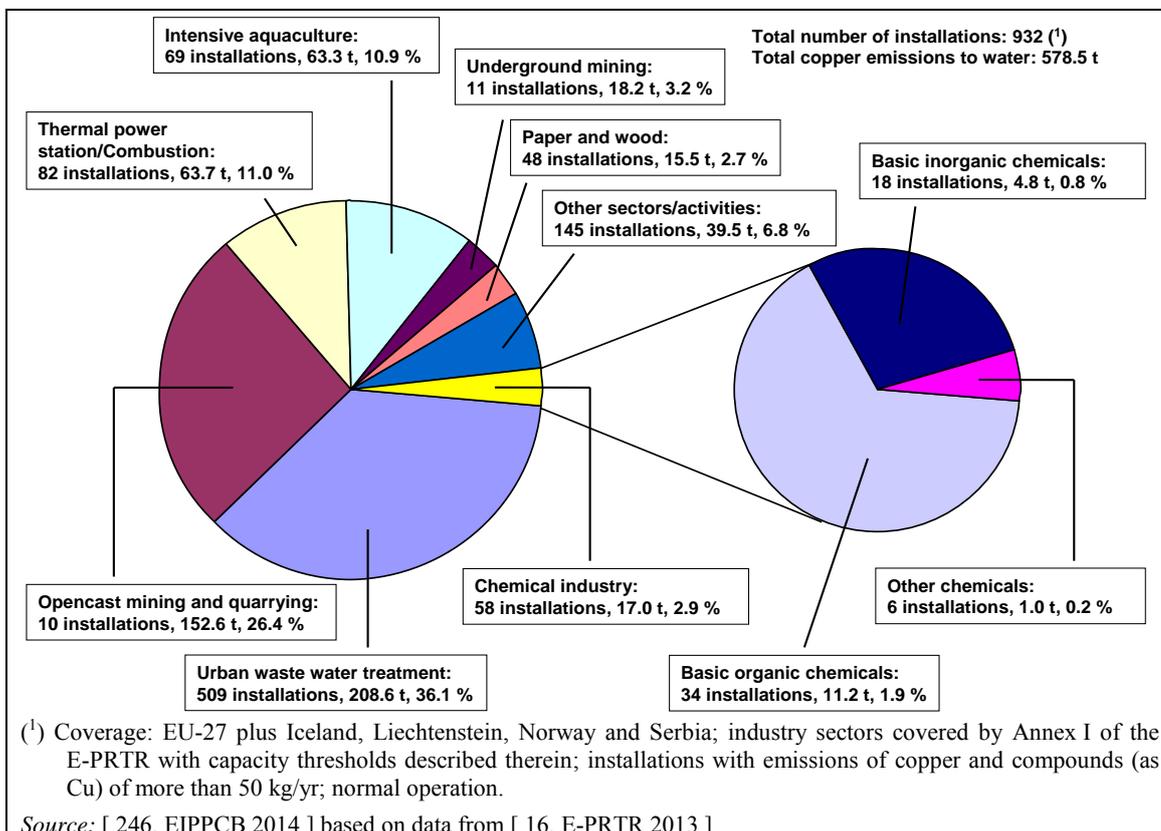
Figure 1.9:   Emissions of copper to water by industry sector/activity in Europe in 2010

1.2.3.8 Mercury

Emissions of mercury to water by industry sector are shown in Figure 1.10. In 2010, 61 installations of the chemical industry sector emitted a total of 1 001 kg of mercury to water, representing 23.5 % of the total amount of mercury emitted to water by all installations covered by the E-PRTR. The largest share of mercury emissions originated from urban waste water treatment plants. Within the chemical industry sector, the production of basic inorganic chemicals was responsible for approximately 60 % of all mercury emissions. Many of the chemical installations with emissions of mercury to water used or still use the mercury cell technique for the production of chlorine and sodium/potassium hydroxide.

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of mercury and compounds (as Hg) of more than 1 kg/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]
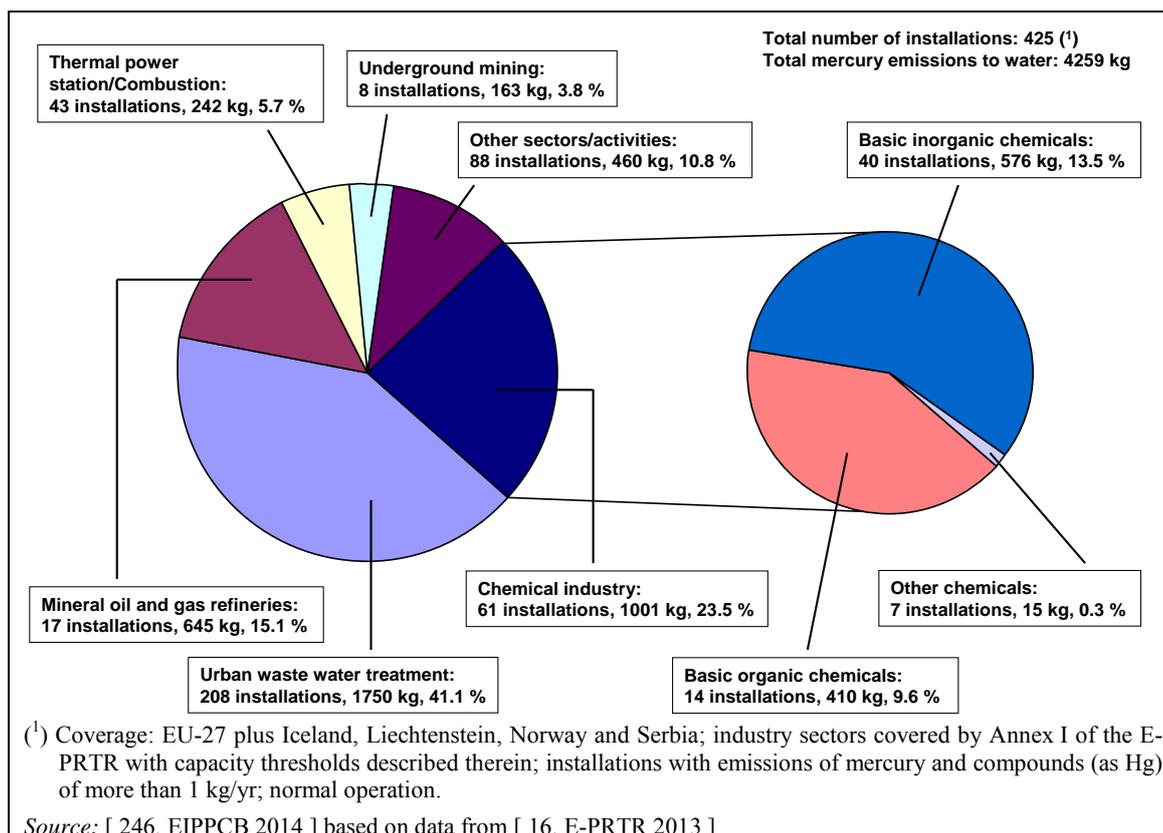
Figure 1.10: Emissions of mercury to water by industry sector/activity in Europe in 2010

1.2.3.9   Nickel

Emissions of nickel to water by industry sector are shown in Figure 1.11. In 2010, 100 installations of the chemical industry sector emitted a total of 24.5 t of nickel to water, representing 7.5 % of the total amount of nickel emitted to water by all installations covered by the E-PRTR. The largest share of nickel emissions originated from urban waste water treatment plants. Within the chemical industry sector, the production of basic organic and inorganic chemicals were together responsible for more than 95 % of all nickel emissions.

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of nickel and compounds (as Ni) of more than 20 kg/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]
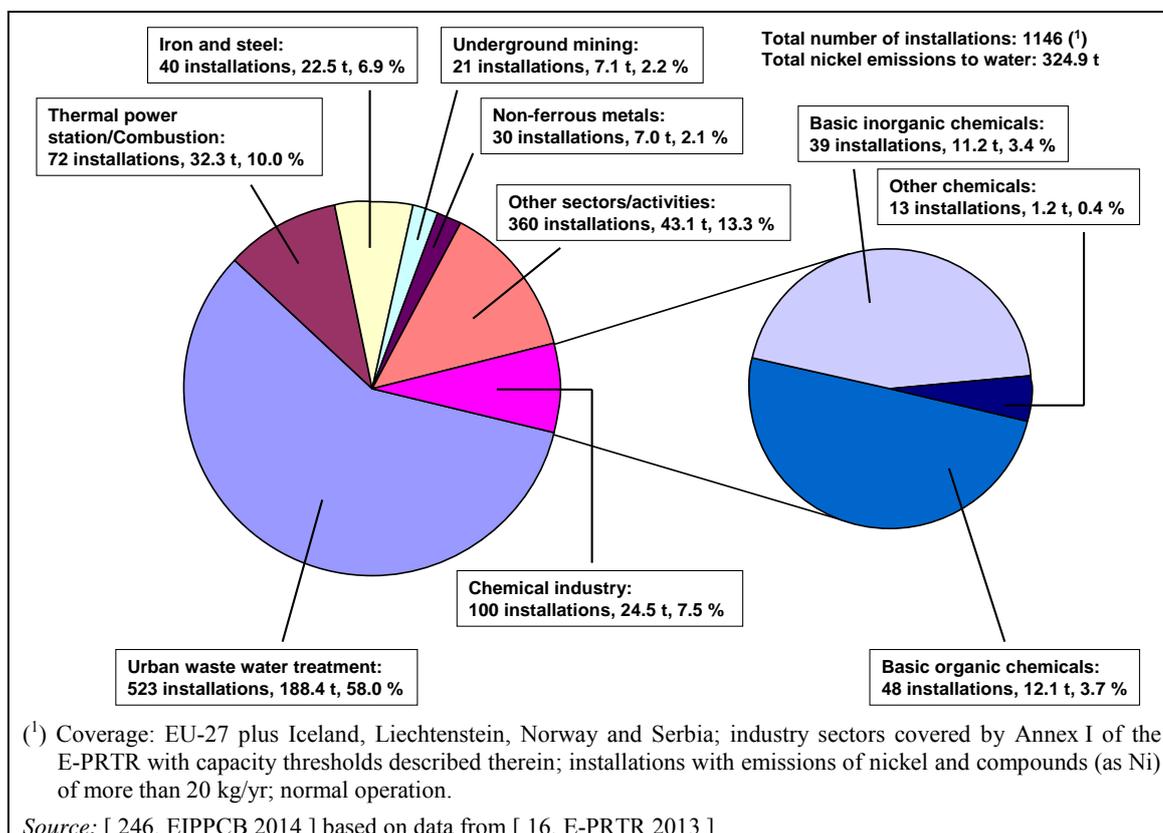
Figure 1.11: Emissions of nickel to water by industry sector/activity in Europe in 2010

1.2.3.10   Lead

Emissions of lead to water by industry sector are shown in Figure 1.12. In 2010, 47 installations of the chemical industry sector emitted a total of 11.8 t of lead to water, representing 6.8 % of the total amount of lead emitted to water by all installations covered by the E-PRTR. The largest share of lead emissions originated from urban waste water treatment plants followed by underground mining. Within the chemical industry sector, the production of basic inorganic chemicals was responsible for more than 75 % of all lead emissions.

Thermal power station/Combustion:
45 installations, 18.0 t, 10.5 %

Iron and steel:
31 installations, 8.6 t, 5.0 %

Total number of installations: 613 ([1])
Total lead emissions to water: 172.2 t

Underground mining:
19 installations, 41.6 t, 24.2 %

Other sectors/activities:
174 installations, 22.2 t, 12.9 %

Basic inorganic chemicals:
26 installations, 9.1 t, 5.3 %

Other chemicals:
6 installations, 0.3 t, 0.2 %

Chemical industry:
47 installations, 11.8 t, 6.8 %

Urban waste water treatment:
297 installations, 70.0 t, 40.7 %

Basic organic chemicals:
15 installations, 2.4 t, 1.4 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of lead and compounds (as Pb) of more than 20 kg/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.12: Emissions of lead to water by industry sector/activity in Europe in 2010

1.2.3.11   Zinc

Emissions of zinc to water by industry sector are shown in Figure 1.13. In 2010, 115 installations of the chemical industry sector emitted a total of 150 t of zinc to water, representing 6.0 % of the total amount of zinc emitted to water by all installations covered by the E-PRTR. The largest share of zinc emissions originated from urban waste water treatment plants. Within the chemical industry sector, the production of basic organic and inorganic chemicals were together responsible for almost 90 % of all zinc emissions.

Iron and steel:
45 installations, 160 t, 6.4 %

Paper and wood:
90 installations, 159 t, 6.3 %

Total number of installations: 1905 (¹)
Total zinc emissions to water: 2513 t

Intensive aquaculture:
565 installations, 182 t, 7.3 %

Thermal power station/Combustion:
86 installations, 116 t, 4.6 %

Basic inorganic chemicals:
30 installations, 73 t, 2.9 %

Other sectors/activities:
260 installations, 249 t, 9.9 %

Underground mining:
44 installations, 260 t, 10.3 %

Chemical industry:
115 installations, 150 t, 6.0 %

Other chemicals:
19 installations, 17 t, 0.7 %

Urban waste water treatment:
700 installations, 1237 t, 49.2 %

Basic organic chemicals:
66 installations, 61 t, 2.4 %

(¹) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of zinc and compounds (as Zn) of more than 100 kg/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.13: Emissions of zinc to water by industry sector/activity in Europe in 2010

1.2.4   Emissions to air

1.2.4.1   Non-methane volatile organic compounds (NMVOC)

The majority of emissions of non-methane volatile organic compounds (NMVOC) in the chemical industry sector are diffuse/fugitive emissions or occur during storage, and both sources are difficult to measure and quantify [15, CEFIC 2012]. NMVOC emissions to air by industry sector are shown in Figure 1.14. In 2010, 226 installations of the chemical industry sector emitted a total of 98.3 kt of NMVOC to air, representing 20.4 % of the total amount of NMVOC emitted to air by all installations covered by the E-PRTR. The largest share of NMVOC emissions originated from mineral oil and gas refineries. Within the chemical industry sector, the production of basic organic chemicals was responsible for almost 75 % of all NMVOC emissions.

Thermal power station/Combustion:
99 installations, 46.6 kt, 9.7 %

Underground mining:
27 installations, 23.5 kt, 6.3 %

Paper and wood:
67 installations, 31.4 kt, 6.5 %

Food and beverages:
37 installations, 15.6 kt, 3.2 %

Other sectors/activities:
116 installations, 39.5 kt, 8.2 %

Total number of installations: 917 (¹)
Total NMVOC emissions to air: 481.3 kt

Basic pharmaceutical products:
55 installations, 18.7 kt, 3.9 %

Surface treatment using organic solvents:
239 installations, 83.3 kt, 17.4 %

Chemical industry:
226 installations, 98.3 kt, 20.4 %

Other chemicals:
19 installations, 6.1 kt, 1.3 %

Mineral oil and gas refineries:
106 installations, 135.7 kt, 28.2 %

Basic organic chemicals:
152 installations, 73.5 kt, 15.3 %

(¹) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of NMVOC of more than 100 t/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.14: Emissions of NMVOC to air by industry sector/activity in Europe in 2010

1.2.4.2   Ammonia

Ammonia emissions to air by industry sector are shown in Figure 1.15. In 2010, 99 installations of the chemical industry sector emitted a total of 18.8 kt of ammonia to air, representing 9.4 % of the total amount of ammonia emitted to air by all installations covered by the E-PRTR. The largest share of ammonia emissions by far originated from the intensive rearing of poultry and pigs. Within the chemical industry sector, the production of basic inorganic chemicals and fertilisers were together responsible for almost 90 % of all ammonia emissions.

Landfills:
16 installations, 3.6 kt, 1.8 %

Cement and lime:
81 installations, 3.2 kt, 1.6 %

Other sectors/activities:
206 installations, 13.3 kt, 6.7 %

Total number of installations: 5803 ([1])
Total ammonia emissions to air: 199.6 kt

Fertilisers:
34 installations, 7.7 kt, 3.8 %

Other chemicals:
32 installations, 2.1 kt, 1.1 %

Chemical industry:
99 installations, 18.8 kt, 9.4 %

Intensive rearing of poultry and pigs:
5401 installations, 160.7 kt, 80.5 %

Basic inorganic chemicals:
33 installations, 9.0 kt, 4.5 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of ammonia of more than 10 t/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.15: Emissions of ammonia to air by industry sector/activity in Europe in 2010

1.2.4.3   Nitrogen oxides

Emissions of nitrogen oxides to air by industry sector are shown in Figure 1.16. In 2010, 215 installations of the chemical industry sector emitted a total of 132 kt of nitrogen oxides to air, representing 5.2 % of the total amount of nitrogen oxides emitted to air by all installations covered by the E-PRTR. The largest share of nitrogen oxide emissions originated from thermal power stations and other combustion installations. Within the chemical industry sector, the production of basic organic chemicals was responsible for almost 60 % of all nitrogen oxide emissions.

Cement and lime:
272 installations, 247 kt, 9.7 %

Glass:
224 installations, 93 kt, 3.7 %

Total number of installations: 2750 ([1])
Total NO$_X$/NO$_2$ emissions to air: 2552 kt

Mineral oil and gas refineries:
114 installations, 151 kt, 5.9 %

Iron and steel:
85 installations, 89 kt, 3.5 %

Basic inorganic chemicals:
67 installations, 35 kt, 1.4 %

Other sectors/activities:
722 installations, 295 kt, 11.6 %

Fertlisers:
27 installations, 20 kt, 0.8 %

Chemical industry:
215 installations, 132 kt, 5.2 %

Other chemicals:
4 installations, 1 kt, 0.0 %

Thermal power station/Combustion:
1118 installations, 1544 kt, 60.5 %

Basic organic chemicals:
117 installations, 76 kt, 3.0 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of nitrogen oxides (NO$_X$/NO$_2$) of more than 100 t/yr; normal operation.

Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.16:   Emissions of nitrogen oxides to air by industry sector/activity in Europe in 2010

1.2.4.4 Sulphur oxides

Emissions of sulphur oxides to air by industry sector are shown in Figure 1.17. In 2010, 111 installations of the chemical industry sector emitted a total of 128 kt of sulphur oxides to air, representing 3.8 % of the total amount of sulphur oxides emitted to air by all installations covered by the E-PRTR. The largest share of sulphur oxide emissions originated from thermal power stations and other combustion installations. Within the chemical industry sector, the production of basic organic and inorganic chemicals were together responsible for approximately 90 % of all sulphur oxide emissions.

Non-ferrous metals:
73 installations, 135 kt, 4.0 %

Iron and steel:
36 installations, 91 kt, 2.7 %

Total number of installations: 1336 ([1])
Total SO$_X$/SO$_2$ emissions to air: 3345 kt

Mineral oil and gas refineries:
105 installations, 375 kt, 11.2 %

Glass:
112 installations, 40 kt, 1.2 %

Basic inorganic chemicals:
45 installations, 51 kt, 1.5 %

Other sectors/activities:
315 installations, 218 kt, 6.5 %

Chemical industry:
111 installations, 128 kt, 3.8 %

Other chemicals:
9 installations, 13 kt, 0.4 %

Thermal power station/Combustion:
584 installations, 2358 kt, 70.5 %

Basic organic chemicals:
57 installations, 65 kt, 1.9 %

([1]) Coverage: EU-27 plus Iceland, Liechtenstein, Norway and Serbia; industry sectors covered by Annex I of the E-PRTR with capacity thresholds described therein; installations with emissions of sulphur oxides (SO$_X$/SO$_2$) of more than 150 t/yr; normal operation.
Source: [246, EIPPCB 2014] based on data from [16, E-PRTR 2013]

Figure 1.17: Emissions of sulphur oxides to air by industry sector/activity in Europe in 2010

1.2.5   Generation of waste

In 2010, 2.5 Gt of waste were generated in the EU-27, comprising both wastes from industrial activities and households (Figure 1.18). The largest share of waste originated from construction, followed by mining and quarrying. The manufacturing industry generated a total of 274 Mt of waste, which was equivalent to 11.0 % of the total waste produced in the EU-27. The chemical industry as part of the manufacturing industry generated 52 Mt of waste, which was equivalent to 2.1 % of the total waste generated in the EU-27.

(^{1}) Coverage: EU-27; sectors/activities as defined in the Statistical Classification of Economic Activities in the European Community (NACE); 'Chemicals' refers to NACE C20 – C22.

Source: [246, EIPPCB 2014] based on data from [23, Eurostat 2013]
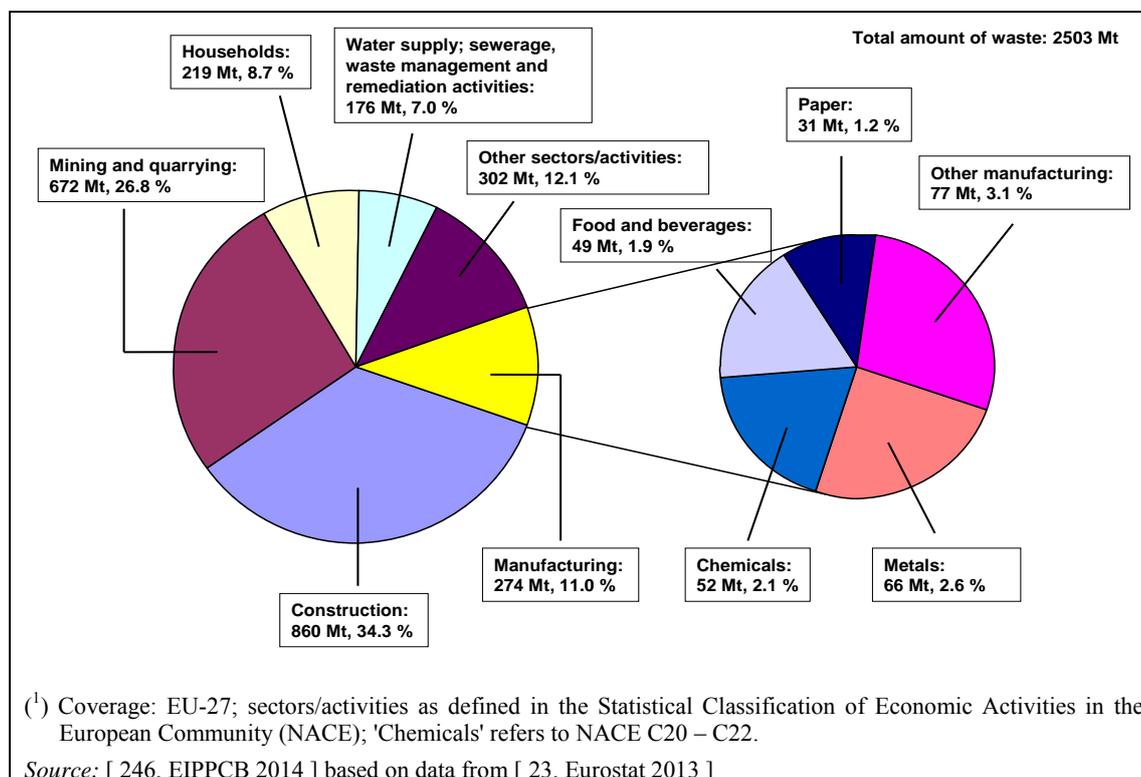
Figure 1.18: Generation of waste by industry sector/activity in the EU-27 in 2010

In 2010, 101.3 Mt of hazardous waste were generated in the EU-27 (Figure 1.19). This represented 4.0 % of the total waste generated. The largest share of hazardous waste, 26.2 Mt, equivalent to 25.8 %, originated from the manufacturing industry. The chemical industry as part of the manufacturing industry generated 7.6 Mt of hazardous waste, which was equivalent to 7.5 % of the total hazardous waste generated in the EU-27.

Services (except wholesale
of waste and scrap):
14.9 Mt, 14.7 %

Total amount of hazardous waste: 101.3 Mt

Water supply; sewerage,
waste management and
remediation activities:
16.4 Mt, 16.2 %

Other sectors/activities:
13.7 Mt, 13.5 %

Chemicals:
7.6 Mt, 7.5 %

Coke and petroleum
products:
4.1 Mt, 4.0 %

Electric and
electronic
products,
motor
vehicles:
2.1 Mt, 2.0 %

Mining and quarrying:
14.0 Mt, 13.8 %

Construction:
16.2 Mt, 16.0 %

Manufacturing:
26.2 Mt, 25.8 %

Metals:
9.6 Mt, 9.5 %

Other manufacturing:
2.8 Mt, 2.8 %

(^{1}) Coverage: EU-27; sectors/activities as defined in the Statistical Classification of Economic Activities in the
European Community (NACE); 'Chemicals' refers to NACE C20 – C22.

Source: [246, EIPPCB 2014] based on data from [23, Eurostat 2013]

Figure 1.19: Generation of hazardous waste by industry sector/activity in the EU-27 in 2010

1.3   Green chemistry

Green chemistry has been defined as 'the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products' [151, Anastas and Warner 1998]. This definition goes beyond the mere production of chemicals, but producers and regulators may need to consider the broader 'life cycle' of chemicals in order to apply holistic environmental protection.

The goal of green chemistry is to reduce the inherent hazards associated with products and processes, whilst maintaining the improvements in the quality of life that the industry has brought. It is not a radical new approach since it builds upon factors that have always been part of process design, but it integrates environmental considerations into the heart of decision-making. Green chemistry has been summarised into twelve principles [151, Anastas and Warner 1998] that have interpreted into the following twelve techniques by the US EPA.

1.   **Prevent waste**; design chemical syntheses to prevent waste, leaving no waste to treat or clean up. It is better to prevent waste than to treat or clean up waste after it is formed (Anastas's first principle).
2.   **Design safer chemicals and products**; design chemical products to be fully effective, yet have little or no toxicity (Anastas's fourth principle).
3.   **Design less hazardous chemical syntheses**; design syntheses to use and generate substances with little or no toxicity to humans and the environment (Anastas's third principle).
4.   **Use renewable feedstocks**; use raw materials and feedstocks that are renewable rather than depleting (Anastas's seventh principle). Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
5.   **Use catalysts, not stoichiometric reagents**; minimise waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once (Anastas's ninth principle).
6.   **Avoid chemical derivative;** avoid using blocking or protecting groups or any temporary modifications, if possible. Derivatives use additional reagents and generate waste (Anastas's eighth principle).
7.   **Maximise atom economy**; design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms. Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product (Anastas's second principle).
8.   **Use safer solvents and reaction conditions**; avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals (Anastas's fifth principle).
9.   **Increase energy efficiency**; run chemical reactions at ambient temperature and pressure whenever possible. Energy requirements should be recognised for the environmental and economic impacts and should be minimised (Anastas's sixth principle).
10.   **Design chemicals and products to degrade after use**; design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment (Anastas's tenth principle).
11.   **Analyse in real time to prevent pollution**; include in-process real-time monitoring and control during syntheses to minimise or eliminate the formation of side products (Anastas's eleventh principle).
12.   **Minimise the potential for accidents**; design chemicals and their forms (solid, liquid, or gas) to minimise the potential for chemical accidents including explosions, fires, and releases to the environment (Anastas's twelfth principle).

1.4 Waste water and waste gas in the chemical industry

1.4.1 Overview

General scientific laws such as chemical and/or physical equilibria make the occurrence of waste inevitable during chemical processes (syntheses) so that unwanted side products have to be expelled. The characteristics and scale of these emissions are highly variable and depend on the composition of the raw materials, products, intermediates, auxiliaries, process conditions, the dimension of the installation, the load situation, the age of the catalyst, etc.

The unwanted outputs occurring during these processes can be divided into three parts:

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

1.4.2 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 synthesis stage are isolated and purified by operations such as filtration and centrifugation from aqueous reaction solutions, or by the work-up of reaction mixtures via, for example, extraction or distillation.

Such waste water streams arising in direct association with chemical syntheses (i.e. process water) include for example:

- mother liquors;
- washing water from the 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 may arise from other on-site sources, such as:

- scrubbing of flue-gases from incineration and combustion;
- conditioning of utility water;
- bleed from boiler feed water systems (probably containing corrosion inhibitors, biocides, and scale);
- blowdown from cooling cycles;
- backwashing of filters;
- laboratory and pilot-scale plants;
- workshops;
- sanitation waste water collection;
- collection of rainwater from contaminated areas;
- washing of production tools or floors;
- accidental product leakages during handling or storage;
- landfill leachates.

The above-mentioned tributary waste water streams contribute to 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 side 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, side 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 [22, BMU/LAWA 2000], 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 % [22, BMU/LAWA 2000].

When considering pollution loads, the ratio is reversed. The higher concentrated tributary waste water streams (10–30 % of the total waste water) generally contain up to 90 % of the relevant contaminant loads [22, BMU/LAWA 2000].

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 limit of detection can be significant in contrast to high concentrations of non-toxic substances. Thus, waste water from chemical industry sites might show toxic effects. Alternatively, synergistic effects of different individual streams, having no toxic effects themselves, might be observed when they are mixed together either in the sewer 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, organic compounds (e.g. BTEX, halogenated organic compounds) and oil;
- the effect and/or hazardous potential for 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 mutagenicity;
- properties such as hydraulic load.

1.4.3   Waste gas

Waste gas streams can roughly be divided into ducted and non-ducted (diffuse) emissions. Only ducted emissions can be treated. As far as diffuse emissions are concerned, the objective of waste gas management is their prevention and/or minimisation. Capturing non-ducted emissions with subsequent treatment can often be carried out in order to minimise pollution.

Emissions to air in the chemical industry include:

- 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, and gas engines;
  ◦ waste gases from emission control equipment, such as filters, incinerators/oxidisers 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 preheating equipment, which are used only in start-up or shutdown operations;
  ◦ discharges from safety relief devices (e.g. safety vents, safety valves);
  ◦ exhaust air from general ventilation systems;
  ◦ exhaust air from vents from captured diffuse sources, e.g. diffuse sources installed within an enclosure or building;

- diffuse emissions (see Glossary) arising from point, linear, surface or volume sources [85, CEFIC 2000], such as:

  ◦ process emissions from the process equipment inherent in running the plant, released from a large surface or through openings;
  ◦ non-ducted emissions (e.g. 'working losses' and 'breathing losses', when not captured and ducted) from storage equipment and during handling operations (e.g. the 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;
  ◦ 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 (CO_2);
- 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 (VOCs) and organosilicon compounds;
- particulate matter (such as dust, soot, alkali, and heavy metals).

1.5 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, for example:

- consideration of possible environmental impact when planning new production or product lines, or planning the enlargement of existing lines (see in particular Section 3.1.5.3.2);
- decisions on (change of) raw materials;
- decisions on the planned production process;
- decisions on the implementation of process-integrated techniques;
- decisions on the production path;
- decisions on the choice of the discharge path;
- decision on the implementation of central or decentralised treatment or control for waste water/waste gas;
- 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/reduction of fugitive emissions through implementation of a leak detection and repair (LDAR) programme (see Section 3.5.4.4).

As can be seen from the few examples above, the rationale for 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 one can operate a complex chemical 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.

A detailed description of waste water/waste gas management systems and tools to implement them is given in Section 3.1.

1.6 Treatment technology

1.6.1 Overview

The different sources of emissions (liquid and/or gas) 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 techniques, such as water reuse, water savings and pollution prevention (see Section 1.6.2);
- end-of-pipe treatment (individual and/or central facilities, see Section 1.6.3).

1.6.2 Process-integrated techniques

Advanced environmental protection is shifting more and more from end-of-pipe techniques (see Section 1.6.3) to process-integrated, or production-integrated, techniques. Process-integrated techniques are a source of significant environmental improvement in both new and existing plants. They are intended to reduce, or even prevent, the production of residues directly at the 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 the input of raw material including water. Disposal costs and the limitations of end-of-pipe treatment can influence this shift toward process-integrated techniques. Although the prevention of waste, and thus the implementation of process-integrated techniques, is becoming increasingly significant, waste treatment techniques will remain essential contributors to the control of emissions into the environment, mainly when process-integrated techniques 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 include:

- creation of new synthesis pathways;
- use of purer or even different feedstocks and process agents (see for example Section 3.3.1.11);
- use of purer or different fuels;
- optimisation of process steps;
- improvement of plant technology, process control and reaction sequence;
- technical adaptations to the process;
- improvement of the use of catalysts and/or solvents;
- recycling of auxiliaries (e.g. washing water, inert gases, solvents, and catalysts);
- immediate recycling of residues during the process;
- use of residues as raw material for other production processes (product integration within and/or outside the location);
- use of residues for energy generation.

Obviously, the development and implementation of completely new pathways for syntheses in existing plants will remain an exception, mostly for economic reasons, and will therefore be mostly carried out in processes used to manufacture 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.

Though, strictly speaking, process-integrated techniques for the reduction of the pollutant discharge via waste water and waste gas are part of the scope of the other chemical BREFs they

are nevertheless mentioned in this document as long as they are generally applicable in chemical production processes. They are in any case items of good management practice and worthy of consideration when implementing a waste water and waste gas management system on a site.

1.6.3 End-of-pipe techniques

1.6.3.1 Overview

Because it is not always possible to prevent pollution at the source, 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.

1.6.3.2 Waste water treatment

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 at the source or in combined streams as well as final treatment of collected waste water before discharge into a receiving water body. The main waste water end-of-pipe treatment techniques and their applicability to control the major contaminants in the chemical industry are shown in Table 1.1. However, it is only indicative and the reader is encouraged to refer to the details given in the specific sections of this document indicated in the table.

Table 1.1: Major waste water contaminants and their respective treatment techniques

Technique	TSS	BOD COD TOC	Refractory COD/TOC	AOX EOX	N total	NH₄-N (NH₃)	PO₄-P	Heavy metals	Sulphides	Sulphate	Phenols	Oil	Acids, alkalis	Section in this document
Neutralisation	(X)							(X)					X	3.3.2.3.2
Grit separation	X													3.3.2.3.3.2
Coagulation/flocculation	X	X (b, q)						X	X			X (b)		3.3.2.3.3.3
Sedimentation	X	(X) (a)						(X) (j)	X (n)					3.3.2.3.3.4
Flotation	X	X (b)						(X) (j)				X		3.3.2.3.3.5
Filtration	X	(X) (a)						(X) (j)						3.3.2.3.3.6
Microfiltration (MF)/ Ultrafiltration (UF)	(X) (c)	(X) (a, q)						X				X		3.3.2.3.3.7
Oil-water separation	X	X										X		3.3.2.3.3.8
Hydrocyclone	X													3.3.2.3.3.9
Electrocoagulation	X	X						X						3.3.2.3.3.10
Chemical precipitation			X				X	X		X				3.3.2.3.4.2
Crystallisation							X	X						3.3.2.3.4.3
Chemical oxidation (pre)		X	X	X					X		X			3.3.2.3.4.4
Wet oxidation with hydrogen peroxide (pre) (ʷ)		X	X	X	X						X			3.3.2.3.4.4.2
Wet air oxidation (pre) (ʷ)		X	X	X							X			3.3.2.3.4.4.3
Chemical reduction								X (t)						3.3.2.3.4.5
Chemical hydrolysis		X		X										3.3.2.3.4.6
Nanofiltration (NF)/Reverse Osmosis (RO)		X	X	X	X	X	X	X			X			3.3.2.3.4.7
Electrodialysis			X											3.3.2.3.4.8
Electrolysis														3.3.2.3.4.9
Adsorption		X (v)	X	X	X	X		X			X	X		3.3.2.3.4.10
Ion exchange		(X) (d)						X		X				3.3.2.3.4.11
Extraction		X	X	X							X			3.3.2.3.4.12
Pertraction		X	X	X							X			3.3.2.3.4.13
Distillation/rectification		X	X	X										3.3.2.3.4.14
Evaporation (ʷ)		(X) (e)		X	X	X	X	X						3.3.2.3.4.15
Pervaporation		X (f)	X (f)	X (f)										3.3.2.3.4.16
Stripping		(X) (f)		X	X	X		X	X (p)		X			3.3.2.3.4.17
Waste water incineration (FT) (ʷ)		X	X	(X) (g)	X	X		(X) (k)			X	X		3.3.2.3.4.18
Anaerobic treatment		X		(X) (h)	(X) (h)			X (l, m)		X				3.3.2.3.5.2

Technique	TSS	BOD COD TOC	Refractory COD/TOC	AOX EOX	N total	NH₄-N (NH₃)	PO₄-P	Heavy metals	Sulphides	Sulphate	Phenols	Oil	Acids, alkalis	Section in this document
Biological removal of sulphur compounds/heavy metals								X	X	X				3.3.2.3.5.3
Aerobic treatment		X		(X) (ʰ)	X	X	X	(X)	X		X			3.3.2.3.5.4
Nitrification/denitrification					X	X								3.3.2.3.5.5
Enhanced biological phosphorus removal							X							3.3.2.3.5.6
Phosphorus removal by chemical precipitation							X							3.3.2.3.5.7
Retention ponds	X	X												3.3.2.3.6.2
Sand filters	X													3.3.2.3.6.3

(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.(ᵐ) Transferred to sludge.
(ⁿ) Colloids.(ᵒ) Ammonia.
(ᵖ) Hydrogen sulphide.(�q) Some macromolecules.
(ʳ) Side effect of ammonia or nitrate removal.(ˢ) Side solubilisation.
(ᵗ) Cr(VI).(ᵘ) Includes nitrification/denitrification and one-step nitrogen removal process of Annamox type.
(ᵛ) Including colour agents, surfactants, nitrocompounds, chlorocompounds, phenols. (ʷ) Techniques applicable on concentrated effluents [148, Degrémont SUEZ 2007].

NB: (FT) = used as a final treatment technique; (pre) = used in particular as a pretreatment, for example before final biological treatment; X = primary application; (X) = secondary application.

Source: [227, CWW TWG 2009]

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 with its advantages and disadvantages, depending on the situation, including:

- decentralised waste water treatment facilities, treating the aqueous effluent at the source and discharging into a receiving water body (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 the source or in combined streams;
- waste water discharge into a municipal WWTP;
- waste water discharge into a municipal WWTP with on-site pretreatment at the source.

The last two bullet points are special situations of the two preceding bullet points respectively.

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

- the operators of the production installations show a more responsible attitude with respect to the effluent when they are made directly responsible for the quality of their own waste water discharge;
- more flexibility exists for works' enlargement or for reacting to changing conditions;
- facilities for treatment at the source are tailor-made and thus normally show better performance levels (however, the initial performance might deteriorate, e.g. when new installations/equipment are put in place or modifications are carried out);
- in contrast to the centralised biological treatments, there is no (or less) excess activated sludge to dispose of;
- the treatment performance of non-biological techniques is independent of the biodegradability of the waste water streams;
- dilution by mixing of different waste water streams can be avoided, normally resulting in a higher treatment efficiency;
- the cost-benefit ratio can be much better in tributary stream treatment than in centralised treatment.

Decentralised waste water treatment is generally the 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) include:

- making use of synergistic effects of 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.

There are instances where waste water from chemical industry sites is also treated together with municipal waste water, either in 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 for 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 neither synergistic nor antagonistic effects on the receiving water, at least as a first approximation [22, BMU/LAWA 2000] (a contrary example of a coordinated operation of a chemical and a municipal WWTP is described in Section 7.1, Annex I). The pollutant loads disposed of are generally additive.

Advantages of joint waste water treatment may include [22, BMU/LAWA 2000]:

- the operational stability of joint biological treatment which can be favourably influenced by:

  ◦ improving the nutrient conditions;
  ◦ optimising the waste water temperature and thus the degradation kinetics;
  ◦ equalising the feed volume and load (see Section 3.3.2.1), 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 which can, in individual cases, realise savings in investment and operating costs.

Disadvantages of joint waste water treatment may include the items listed below.

- 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 [22, BMU/LAWA 2000].
- 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 the waste water streams coming from the industrial part carefully for any inhibiting or disturbing factors [22, BMU/LAWA 2000].
- 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 are discharged without degradation into a receiving water body, adsorbed onto the activated sludge and/or stripped into the atmosphere during aeration. This would counteract the obligation to prevent or control these substances at the source. This disadvantage affects all treatment actions on combined waste water streams.
- Combined treatment may result in sludge that is too contaminated for further usage or further treatment, e.g. by anaerobic digestion.

The joint treatment of municipal and chemical industry waste water necessitates appropriate buffer tanks to cope with excess rain in the event of heavy rainfall in order to avoid hydraulic overload, which might lead to increased pollutant discharge accompanied by loss of bacteria from the activated sludge compartment of the WWTP [22, BMU/LAWA 2000].

Another important aspect of the waste water system is the handling of uncontaminated rainwater and cooling water. In a number of older chemical sites 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 have a separate sewer system for the collection of uncontaminated rainwater and cooling water. Details are given in Section 3.3.2.3.6.

1.6.3.3   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;
- odour.

Waste gas treatment normally takes place directly at the 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 compounds 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 compounds and the generally large volumes that are handled and processed, safety is a crucial issue. Moreover, facilities needed to transport waste gases through a whole site require significant investments and can be technically challenging.

A selection of techniques by pollutant is given in Table 1.2, and by waste gas flow rate in Table 1.3.

Table 1.2:   Selection of techniques for waste gas emission reduction by pollutant to be removed

Technique	Dry matter	Wet matter	Inorganic particulates	Organic particulates	Inorganic gaseous or vaporous compounds	Organic gaseous or vaporous compounds	Odour	Section in this document
Recovery and abatement for VOCs and inorganic compounds								
Membrane separation (pre)						X		3.5.1.2.1
Condensation (pre)					(X)	X		3.5.1.2.2
Cryocondensation (pre, FT)					(X)	X	(X)	3.5.1.2.2
Adsorption (FT, pol)					X	X	X	3.5.1.2.3
Wet gas scrubber (water) (FT)	(X)	(X)	(X)	(X)	X	X	X	3.5.1.2.4
Wet gas scrubber (alkaline) (FT)	(X)	(X)	(X)	(X)	X	X	X	3.5.1.2.4
Wet gas scrubber (alkaline oxidative) (FT)	(X)	(X)	(X)	(X)			X	3.5.1.2.4
Wet gas scrubber (acidic) (FT)	(X)	(X)	(X)	(X)	X	X	X	3.5.1.2.4
Abatement for VOCs and inorganic compounds								
Biofiltration (FT)					X	X	X	3.5.1.3.1
Bioscrubbing (FT)					X	X	X	3.5.1.3.2
Biotrickling (FT)					X	X	X	3.5.1.3.3
Moving-bed trickling filter (FT)					X	X	X	3.5.1.3.4
Thermal oxidation (FT)				X		X	X	3.5.1.3.5
Catalytic oxidation (FT)						X	X	3.5.1.3.6
Ionisation (FT)						X	X	3.5.1.3.7
Photo/UV oxidation (FT)						X	X	3.5.1.3.8
Recovery and abatement for particulates								
Settling chamber/gravitational separator (pre)	X	X	X	X				3.5.1.4.2
Cyclone (pre)	X	X	X	X				3.5.1.4.3
Electrostatic precipitator (FT)	X	X	X	X	(X)	(X)		3.5.1.4.4
Wet dust scrubber (FT)	X	X	X	X				3.5.1.4.5
Fabric filter (FT)	X		X	X				3.5.1.4.6
Ceramic and metal filter (FT)	X		X	X				3.5.1.4.7
Catalytic filtration (FT)	X	X	X	X		X		3.5.1.4.8
Two-stage dust filter (pol)	X		X	X				3.5.1.4.9
Absolute (HEPA) filter (pol)	X		X	X				3.5.1.4.10
High-efficiency air filter (pol)		X						3.5.1.4.11
Mist filter (pre, pol)		X			(X)			3.5.1.4.12
Recovery and abatement for inorganic compounds								
Dry alkali injection (FT)					X			3.5.1.5.2
Semi-dry alkali injection (FT)					X			3.5.1.5.2
Wet lime injection (FT)					X			3.5.1.5.2
SNCR (FT)					X			3.5.1.5.3
SCR (FT)					X	(X)		3.5.1.5.3
NSCR (FT)					X			3.5.1.5.4
Wet gas scrubber for NO_X (FT)					X			3.5.1.5.5
Flaring								
Flaring (FT)						X	X	3.5.1.6

NB: (FT) = treatment technique used as a final treatment technique; (pol) = mainly used as a polishing technique after application of a standard technique; (pre) = mainly used as a pretreatment; X = primary application; (X) = secondary application.

Source: [176, Schenk et al. 2009]

Table 1.3: Selection of techniques for waste gas emission reduction by waste gas flow rate

Technique	100 (Nm³/h)	1 000 (Nm³/h)	10 000 (Nm³/h)	100 000 (Nm³/h)	Section in this document
Recovery and abatement for VOCs and inorganic compounds					
Membrane separation					3.5.1.2.1
Condensation	X	X	XX	X	3.5.1.2.2
Cryocondensation	X	X			3.5.1.2.2
Adsorption	X	XX	XX	X	3.5.1.2.3
Wet gas scrubber (water)	X	X	XX	XX	3.5.1.2.4
Wet gas scrubber (alkaline)	X	X	XX	XX	3.5.1.2.4
Wet gas scrubber (alkaline oxidative)	X	X	XX	X	3.5.1.2.4
Wet gas scrubber (acidic)	X	X	XX	XX	3.5.1.2.4
Abatement for VOCs and inorganic compounds					
Biofiltration	X	XX	XX	XX	3.5.1.3.1
Bioscrubbing	X	X	X	X	3.5.1.3.2
Biotrickling	X	X	X	X	3.5.1.3.3
Moving-bed trickling filter		X	X		3.5.1.3.4
Thermal oxidation		X	XX		3.5.1.3.5
Catalytic oxidation		X	XX		3.5.1.3.6
Ionisation	X	X	X	X	3.5.1.3.7
Photo/UV oxidation		X	X		3.5.1.3.8
Recovery and abatement for particulates					
Settling chamber/gravitational separator	X	X	XX	XX	3.5.1.4.2
Cyclone	X	XX	XX	X	3.5.1.4.3
Electrostatic precipitator (one-stage)			X	X	3.5.1.4.4
Wet dust scrubber		X	XX	XX	3.5.1.4.5
Fabric filter	X	X	XX	XX	3.5.1.4.6
Ceramic filter		XX	X	X	3.5.1.4.7
Metal filter	NI				3.5.1.4.7
Catalytic filtration	X	X	X		3.5.1.4.8
Two-stage dust filter		X	X		3.5.1.4.9
Absolute (HEPA) filter	X	X			3.5.1.4.10
High-efficiency air filter (HEAF)	XX	XX	X		3.5.1.4.11
Mist filter		X	XX	XX	3.5.1.4.12
Recovery and abatement for inorganic compounds					
Dry alkali injection			XX	X	3.5.1.5.2
Semi-dry alkali injection			X	XX	3.5.1.5.2
Wet lime injection		X	X	X	3.5.1.5.2
SNCR	X	X	X	X	3.5.1.5.3
SCR		X	XX	XX	3.5.1.5.3
NSCR			X		3.5.1.5.4
Wet gas scrubber for NO$_X$			X		3.5.1.5.5
Flaring					
Flaring	X	X	X	X	3.5.1.6
NB: NI = No information provided; X = application; XX = most common applications.					
Source: [176, Schenk et al. 2009]					

1.7 Cross-media effects 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 (VOCs) and volatile inorganic compounds (e.g. ammonia, hydrogen sulphide). Whenever these water flows are open to the atmosphere, (odorous) emissions of these compounds may occur. Special attention is usually paid to aeration of biological waste water treatment basins, stirring operations, open buffer tanks, settling tanks and waste water stripping facilities. In all of these cases, the emission of pollutants can be shifted from the water compartment to the air. Thus additional waste gas treatment can be necessary. Emissions to air 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 environment is briefly reviewed in Table 1.4.

Table 1.4: Potential impact of waste water treatment facilities on the environment

Environmental compartment	Potential effect/emission
Air	• Evaporation/formation of odour (e.g. H_2S, NH_3, mercaptans) • Formation of aerosols • Drift of potentially hazardous microorganisms 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, a significant reduction of emissions to water • When rainwater is treated together with process water, the treatment system might get overloaded in the event of heavy rainfall, which can cause additional pollutant emissions because the treatment system cannot function properly
Waste	• Waste water treatment sludge and scrubber solutions
Other	• The WWTP plant consumes energy. In some cases, biogas is generated and can be used as a source of energy • Consumption of auxiliary chemicals (e.g. nutrients such as phosphorus, flocculating agents such as iron salts)
Source: [24, InfoMil 2000]	

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, see Section 3.4.2) account for a significant part of the energy requirements 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 (see Section 3.3.2.3.5.2), for example, the gas generated by treatment (biogas) can be used as a fuel. Otherwise it needs to be flared (see Section 3.5.1.6). Waste gases from flaring are usually not treated.

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 water and air. The use of wet scrubbing (see Section 3.5.1.4.5), for example, means that waste water has to be treated in a subsequent treatment step. Waste gas oxidation (see in particular Sections 3.5.1.3.5 and 3.5.1.3.6) discharges a flue-gas which contains 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.

Table 1.5:   Potential impact of waste gas treatment facilities on the environment

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 the 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 • Consumption of auxiliary chemicals (e.g. ammonia for selective non-catalytic reduction (SNCR), alkaline agents for scrubbing solutions)

In addition to flares (see Section 3.5.1.6) and thermal/catalytic oxidisers (see Sections 3.5.1.3.5 and 3.5.1.3.6), 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 and/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 fabric filters (see Section 3.5.1.4.7), waste water generated by scrubbers (see Section 3.5.1.4.5) 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. 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. The Reference Document on Economics and Cross-media Effects (ECM) describes methodologies that can help to determine the break-even point, where the positive effects outweigh the negative effects of a treatment measure [112, COM 2006].

In summary, waste water and waste gas treatment, in addition to their individual impacts on the environment, affect each other in the following 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 techniques result in gaseous and/or liquid releases, which need further waste gas and/or waste water treatment;
- each release (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 flue-gases or stripping of volatile material from WWTPs.

2 CURRENT EMISSION AND CONSUMPTION LEVELS OF WASTE WATER TREATMENT PLANTS

2.1 General information on the surveys

This chapter summarises the installation-specific data gathered during two surveys carried out over the course of the BREF review process (for the schedule see Table 6.1). The first survey mostly covered waste water treatment plants (WWTPs) on larger integrated sites while the second covered to a greater extent WWTPs on smaller sites with limited production activities ('stand-alone' installations). The second survey also served to update and complement data from the first survey.

Overall, questionnaires for 122 installations were submitted to the EIPPCB. Subsequently, the EIPPCB sent numerous requests for clarification and additional information to the TWG which resulted in many corrections. Some 15 questionnaires were discarded because the WWTP was outside the scope of this BREF, the questionnaire contained too few data, or because questionnaires had been sent in duplicate. Following this data cleansing, a total of 107 questionnaires were taken into account for further analysis. Of these, 35 installations participated only in the first survey, 46 only in the second, and 26 in both surveys (see Table 2.1).

Table 2.1: Overview of the installations which participated in the surveys

Location	Number of installations				Share
	Only 1st survey	Only 2nd survey	Both surveys	Total	
AT	0	1	1	2	1.9 %
BE	1	1	5	7	6.5 %
CZ	0	0	3	3	2.8 %
DE	9	1	12	22	20.6 %
DK	0	4	0	4	3.7 %
ES	5	6	1	12	11.2 %
FR	5	5	3	13	12.1 %
IE	0	1	0	1	0.9 %
IT	5	3	0	8	7.5 %
NL	1	0	0	1	0.9 %
PL	0	6	0	6	5.6 %
SE	1	5	0	6	5.6 %
UK	8	13	1	22	20.6 %
All	**35**	**46**	**26**	**107**	**100 %**
Source: [222, CWW TWG 2013]					

General information on the characteristics of these WWTPs can be found in Table 7.1 in Section 7.2, Annex II.

The share of the EU-27 chemical industry sales in 2011 per country versus the share of the questionnaires per country is shown in Figure 2.1. All EU Member States with major chemical production activities were represented in the surveys. It appears as if some EU Member States were overrepresented (e.g. DK, PL, SE, UK), while others were underrepresented (e.g. DE, FR, IT, NL). However, such an interpretation might prove wrong if the structure of the chemical industry differs from one country to another. For example, the German WWTPs for which questionnaires were submitted were on average larger than those located in the United Kingdom (see Figure 2.6). It would have been better to use the share of chemical installations per country for Figure 2.1, but unfortunately these data were not available.

Source: [246, EIPPCB 2014] based on data from [2, CEFIC 2012] and [222, CWW TWG 2013]
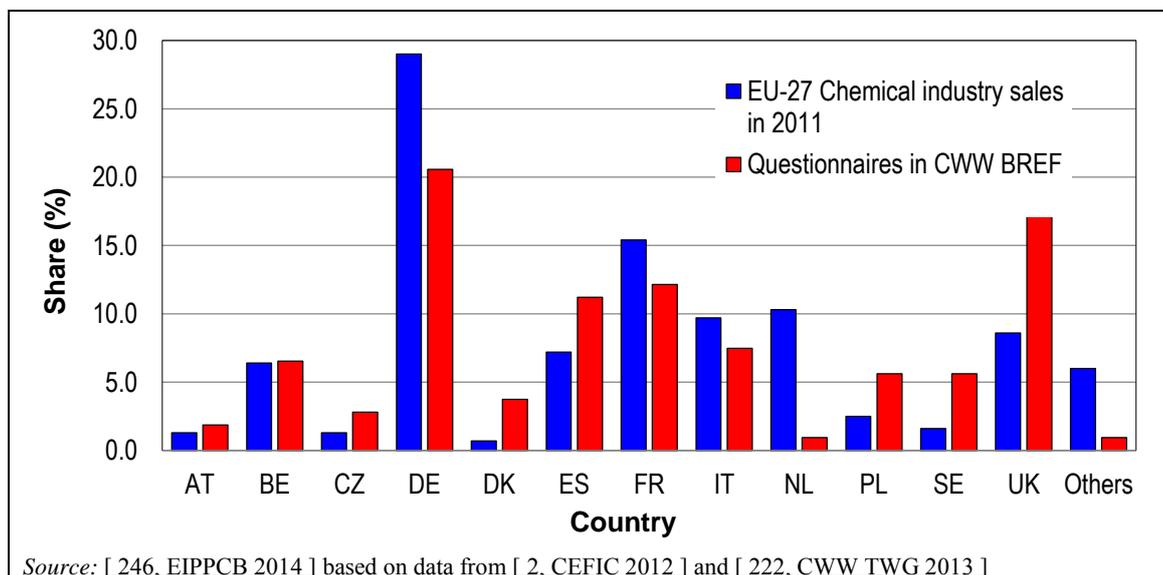
Figure 2.1: **Share of chemical sales per country versus share of questionnaires per country**

Of the questionnaires, 95 concern WWTPs that discharge directly to a receiving water body, while 12 concern indirect discharges, corresponding to 89 % and 11 %, respectively (see also Table 7.1 in Section 7.2, Annex II). Approximately two thirds of the direct discharges were to freshwater environments (mostly rivers) and one third to marine/estuarine environments. Most of the indirect discharges were to municipal WWTPs (Figure 2.2).

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
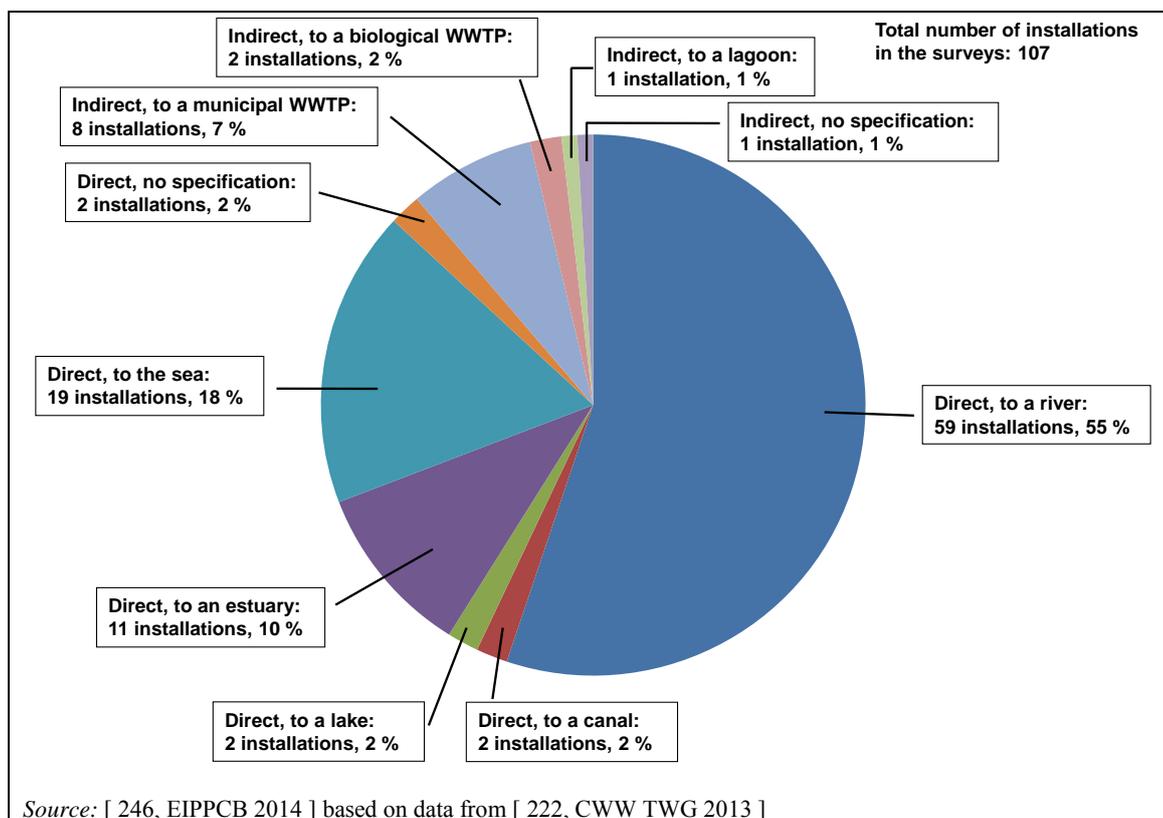
Figure 2.2: **Repartition of WWTPs according to the type of discharge**

Of the 95 directly discharging WWTPs, 60 % treat waste water originating from IED installations from the organic chemistry sector (i.e. LVOC, OFC, POL), 16 % from the inorganic chemistry sector (i.e. LVIC-AAF, LVIC-S, SIC, CAK), and 23 % from both sectors (Figure 2.3).
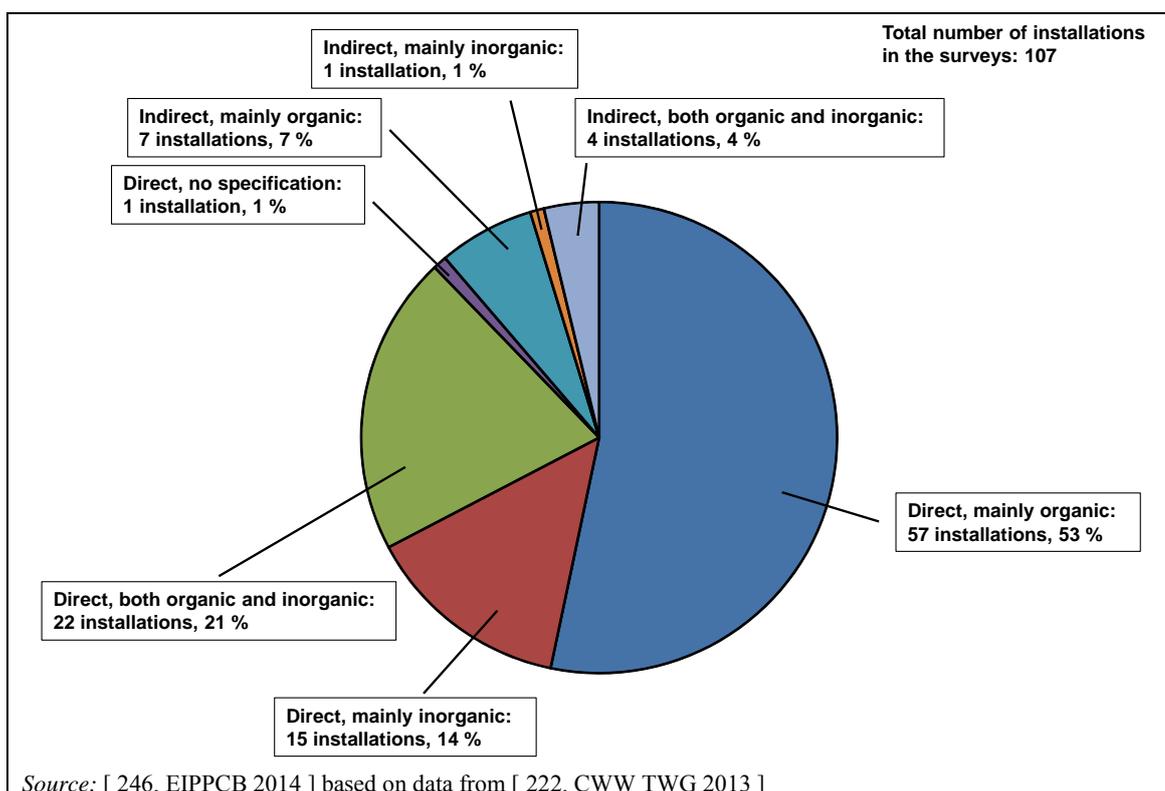
Figure 2.3: **Repartition of WWTPs according to the production activities**

The co-treatment of domestic waste water on the site was reported for 24 out of the 95 directly discharging WWTPs (or 25 %). The domestic waste water originated from sanitary facilities on site and/or from municipalities. Of these 24 WWTPs, 20 provided figures that allowed the volume share of the co-treated domestic waste water to be calculated (Figure 2.4).

NB: Data from 2005 to 2011.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
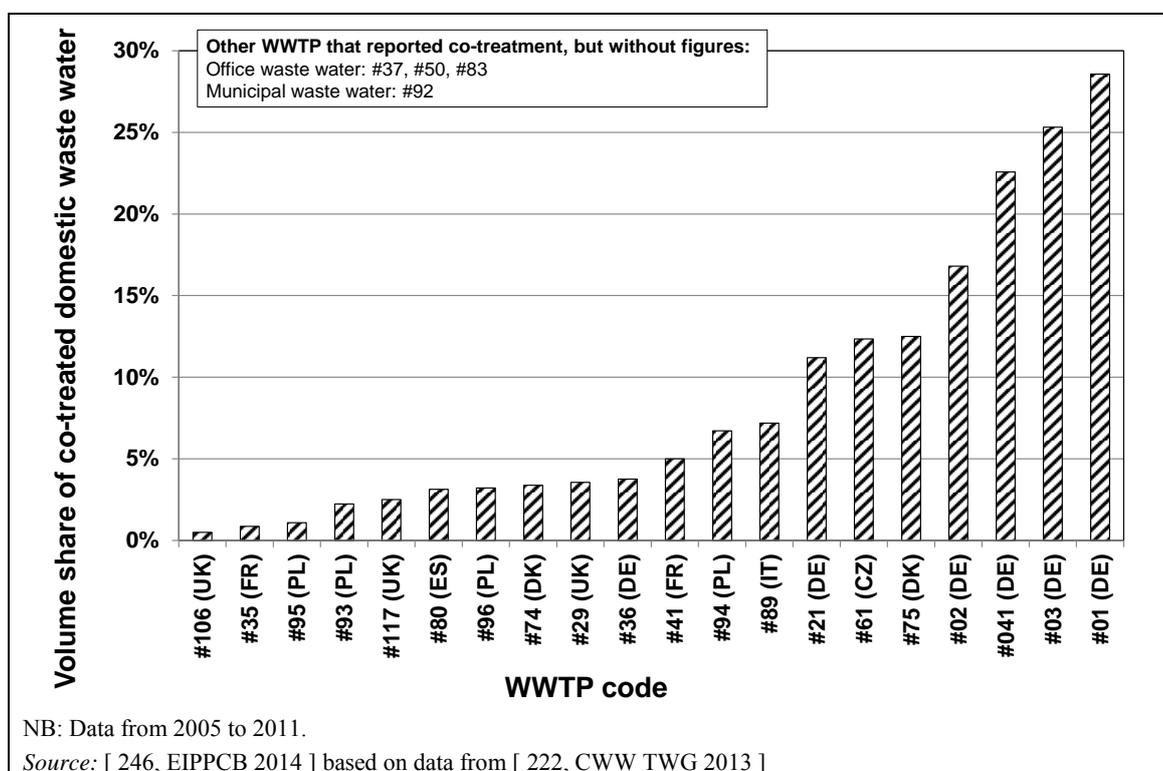
Figure 2.4: **Volume share of co-treated domestic waste water**

The volume share of the co-treated domestic waste water was in all cases below 30 %. The four WWTPs with the highest volume share of domestic waste water (between 17 % and 29 %) are all located in Germany. Information on the corresponding shares of the pollutant loads was not provided with the questionnaires. However, given the generally high concentrations of organic compounds in the influents to the WWTPs with co-treatment (e.g. #01: COD = 3.3 g/l; #02: COD = 1.2 g/l; #03: COD = 0.57 g/l; #041: COD = 1.0 g/l; #21: COD = 2.3 g/l; #75: TOC = 1.9 g/l), it can be reasonably assumed that the main COD load of the plants of the surveys did not originate from domestic waste water.

The questionnaires reflect different sizes of WWTPs, from relatively small WWTPs treating less than 10×10^3 m^3/yr to large WWTPs treating volumes of more than $20\,000 \times 10^3$ m^3/yr (Figure 2.5).The median accounted for approximately $1\,400 \times 10^3$ m^3/yr. The different sizes of the WWTPs are also reflected in the COD influent loads, ranging from approximately 100 t/yr to 145 000 t/yr. Among the directly discharging WWTPs with biological treatment, the lowest volume of treated waste water was reported for WWTP #52 (120×10^3 m^3/yr in 2007), the lowest BOD$_5$ load in the influent for WWTP #62 (34 t/yr = 1 600 p.e. (population equivalent) in 2007), and the highest volume of treated waste water together with the highest BOD$_5$ load in the influent for WWTP #02 ($122\,000 \times 10^3$ m^3/yr and 78×10^3 t/yr = 3.6×10^6 p.e., respectively, in 2007) [222, CWW TWG 2013].

NB: Data from 2007 to 2011. For each installation, the most recent data were used.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
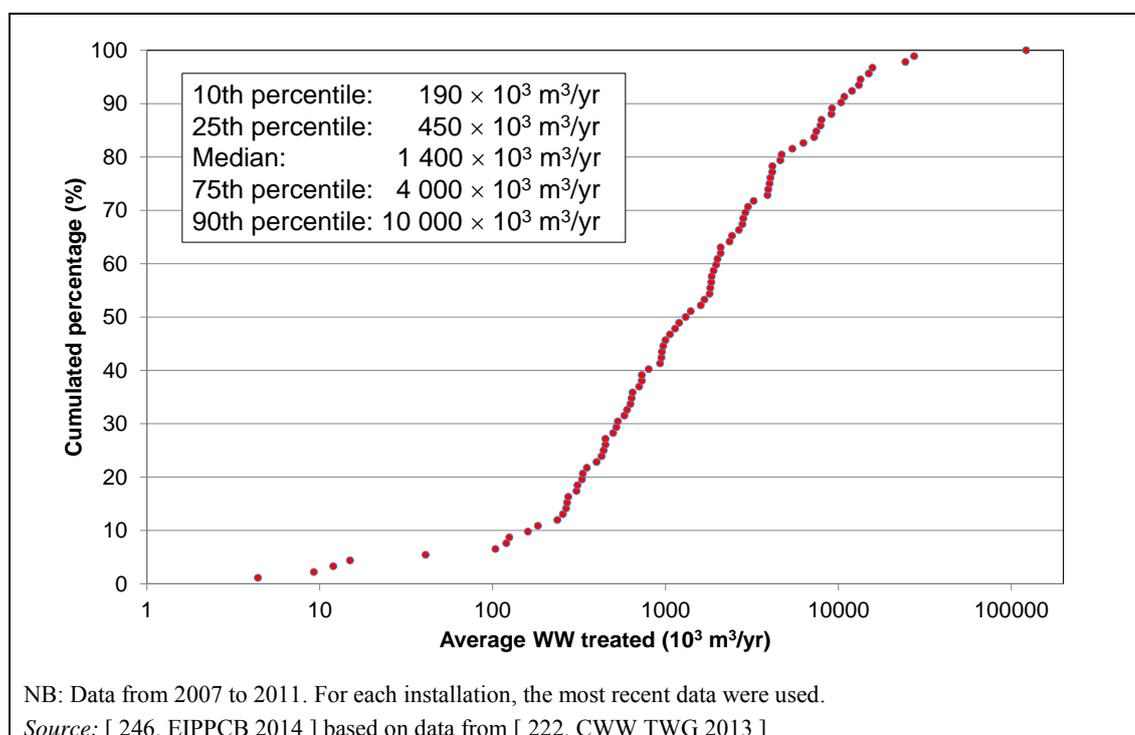
Figure 2.5: **Average waste water volume treated (only direct discharges)**

Further analysis of the questionnaires reveals that, among others, Germany, Italy and Poland were represented by larger WWTPs in the survey, while Belgium, France, Sweden and the United Kingdom were represented by smaller WWTPs (Figure 2.6).

NB: Data from 2007 to 2011. For each installation, the most recent data were used. Three installations with direct discharge did not report the treated waste water volume.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
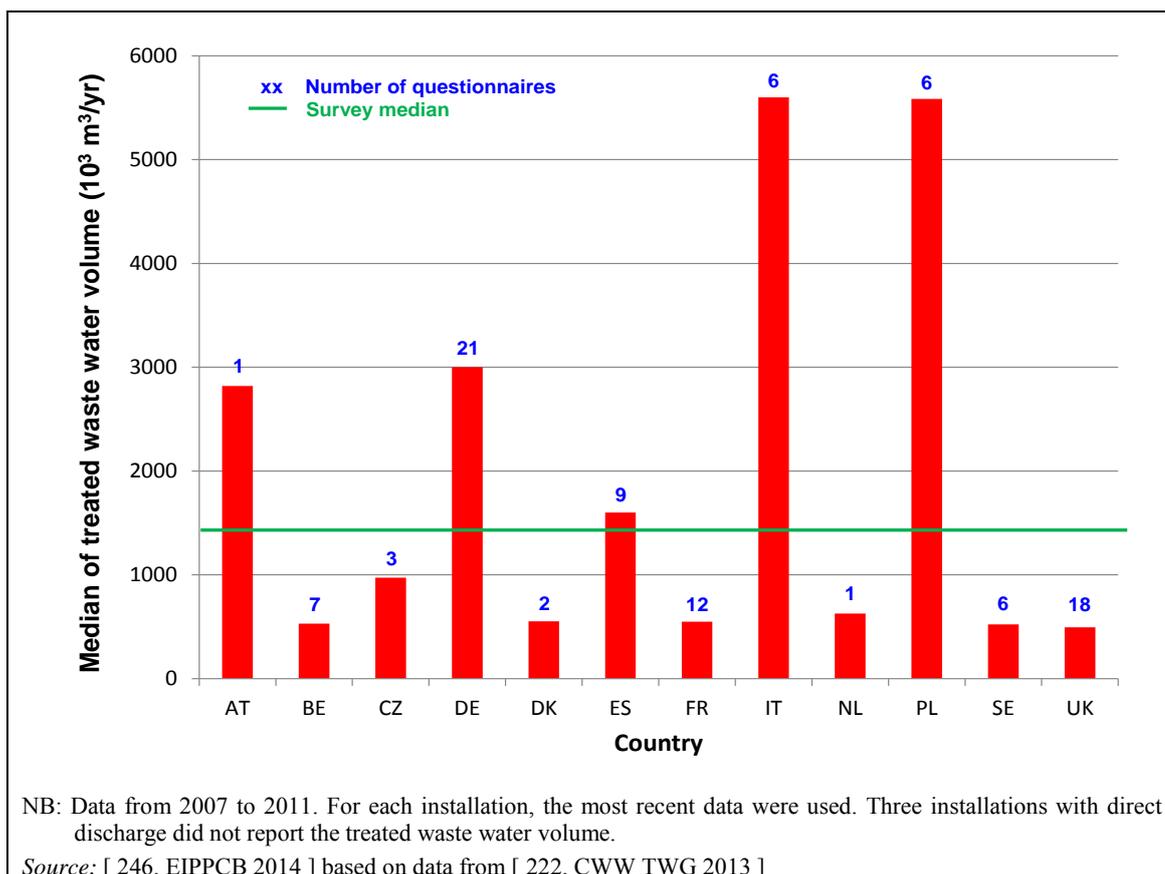
Figure 2.6: **Median of the average waste water volumes treated by the WWTPs of different countries (only direct discharges)**

2.2   Main unit processes at the WWTPs

In order to compare emission levels from the various installations, the techniques used were grouped. Final waste water treatment is usually a combination of individual treatment steps. For example, the most commonly used activated sludge process is generally preceded and followed by a solids removal step. The activated sludge process may be combined with nitrification/denitrification and/or chemical phosphorus precipitation depending on the composition of the waste water. The heterogeneous combinations and, in addition, the different denominations used in the questionnaires for the same technique made it difficult to group installations.

The complete mix activated sludge (CMAS) process was identified as the main final unit process for waste waters with organic substances (53 WWTPs out of a total of 107 WWTPs covered by the surveys). The installations using the CMAS process were then further categorised according to:

- use of flat tanks, tower biology, or membrane bioreactor;
- solids removal techniques;
- pretreatment steps, e.g. anaerobic step, additional activated sludge process, physico-chemical treatments;
- occurrence of nitrogen and/or phosphorus removal.

The main unit processes used at the final WWTPs of the surveys are (see also Table 7.1 in Section 7.2, Annex II):

- physico-chemical and biological treatment or only biological treatment (68 WWTPs):

   ◦ CMAS flat tank (i.e. #01, #02, #03, #041, #06, #09, #10, #11, #12, #14, #17, #18, #19, #22, #24, #25, #28, #37, #40, #47, #48, #49, #50, #51, #52, #54, #57, #58, #60, #61, #62, #63, #64, #68);
   ◦ CMAS tower biology (i.e. #07, #13, #14, #15, #16, #21, #45);
   ◦ membrane bioreactor (i.e. #08, #36, #41 (partially), #69, #70 (partially), #118);
   ◦ activated sludge without further specification (i.e. #41, #70, #75, #83, #91, #96, #102, #103, #104, #108);
   ◦ fixed-bed reactor (i.e. #29);
   ◦ expanded-bed process (i.e. #33, #34);
   ◦ biological treatment without further specification (i.e. #74, #76, #82, #89, #90, #92, #98, #100, #101, #105);

- physico-chemical treatment only (38 WWTPs):

   ◦ neutralisation (i.e. #042, #27, #35, #56, #65, #66, #67, #73, #79, #80, #81, #84, #93, #94, #106, #107, #109, #110, #111, #113, #115, #116, #117, #120, #121);
   ◦ precipitation/coagulation/flocculation (i.e. #042, #05, #27, #32, #35, #56, #73, #93, #115);
   ◦ crystallisation (i.e. #05);
   ◦ skimming (i.e. #53);
   ◦ oil-water separation (i.e. #26, #35, #46, #85);
   ◦ oxidation with H_2O_2 (i.e. #65, #66, #67, #84);
   ◦ stripping (i.e. #27, #38);
   ◦ activated carbon filtration (i.e. #81).

One WWTP (i.e. #88) did not report which techniques are used.

With respect to the final solids (TSS) removal step, the following techniques are applied at the WWTPs:

- sedimentation (i.e. #02, #03, #041, #042, #06, #07, #09, #12, #13, #14, #15, #16, #17, #18, #19, #22, #24, #25, #26, #27, #28, #31, #37, #40, #41, #47, #48, #49, #52, #53, #54, #56, #57, #62, #63, #65, #66, #67, #68, #70, #79, #82, #86, #87, #89, #91, #93, #94, #100);
- ultrafiltration, including membrane bioreactor (i.e. #08, #36, #38, #41 (partially), #69, #70 (partially), #118);
- sand filtration (i.e. #01, #32, #34, #45, #61, #115, #120);
- filtration without further specification (i.e. #05, #105, #117);
- flotation (i.e. #10, #11, #21, #29, #33, #35, #46, #50, #51, #60, #64, #75);
- reverse osmosis (i.e. #58).

Filtration and flotation are often preceded by a sedimentation step.

Depending on the organic load of the influent, a variety of pretreatment processes are used, including:

- additional activated sludge processes (i.e. #01, #041, #08, #09, #10, #14, #33, #41, #61, #63, #70);
- trickling filters (i.e. #07, #57);
- fixed-bed reactors (i.e. #24);
- anaerobic pretreatment (i.e. #16, #29);
- oxidation (i.e. #18, #58);
- oil-water separation (i.e. #45, #89, #90);
- stripping (i.e. #118).

Installation #06 uses waste water incineration for some segregated streams (10 % of the waste water volume and 50 % of the TOC load).

Several of the WWTPs apply nitrogen and/or phosphorus removal. For some WWTPs, nitrogen and/or phosphorus removal were not explicitly mentioned but could be derived from the influent and effluent data:

- nitrification/denitrification (i.e. #01, #02, #03, #041, #06, #07, #08, #09, #10, #11, #12, #14, #16, #21, #22, #34, #36, #37, #40, #41, #45, #49, #50, #52, #57, #58, #60, #61, #63, #69, #70, #74, #75, #82, #89, #92, #96, #98, #100, #108, #118);
- chemical phosphorus precipitation (i.e. #01, #02, #03, #06, #07, #08, #10, #11, #12, #13, #14, #33, #34, #36, #51, #57, #70, #74, #76, #95).

2.3   Energy consumption of biological WWTPs

Data on energy consumption were only gathered during the first survey, but not during the second. For 21 out of a total of 47 biological WWTPs participating in the first survey (directly or indirectly discharging), energy consumption values in combination with waste water volumes and abated COD loads were reported so that specific energy consumption values could be calculated (Figure 2.7). Installations #08, #36, #41 and #69 use membrane bioreactors, which explains their higher specific energy consumption.
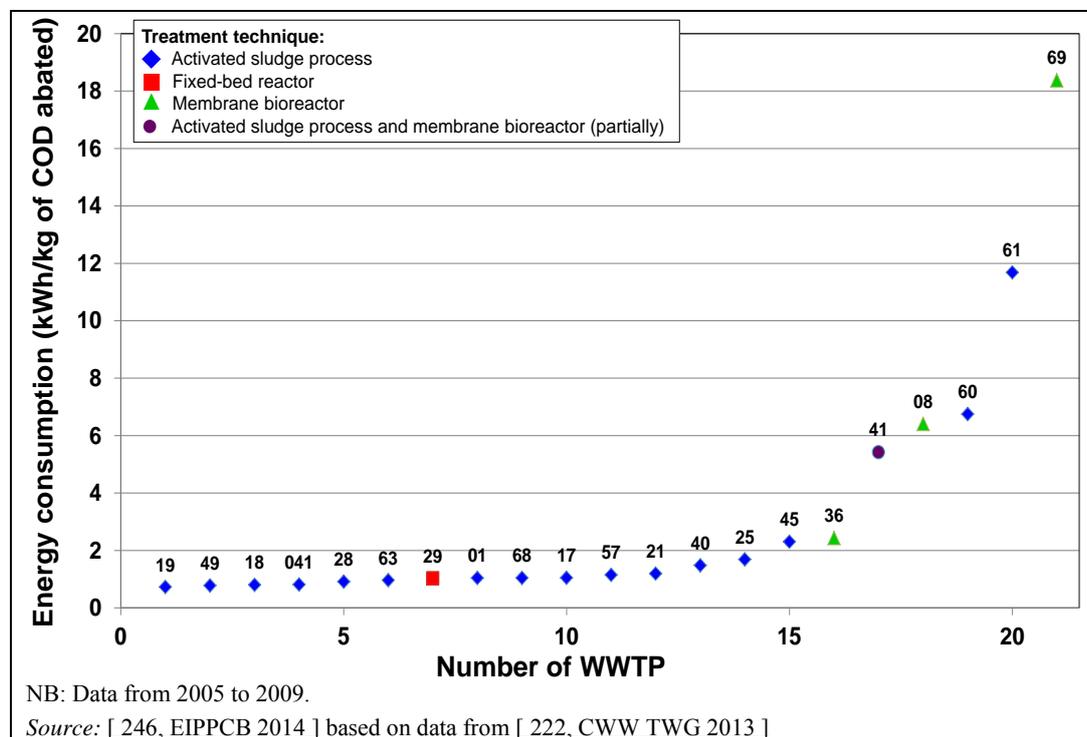
Figure 2.7:   Specific energy consumption of the biological WWTPs

2.4   Analysis of key parameters

2.4.1   General

The following sections discuss the reported performance of the WWTPs over a number of parameters. The graphs contained in Section 2.4 exclusively refer to directly discharging WWTPs. Influent and effluent data were gathered for the reference years 2007 to 2011. In general, the most recent dataset of each WWTP is displayed except in a few cases, where the dataset of one of the preceding years was more complete (i.e. #041, #042, #10, #29, #86, #87, #100). The symbols used in this section are given in Table 2.2.

Table 2.2:   Symbols used in the graphs of Section 2.4

Average values		
Symbol	**Waste water (WW) stream**	**Type of discharge and waste water treated**
▲	Effluent	Direct discharge, organic WW
▲		Direct discharge, organic and inorganic WW
▲		Direct discharge, inorganic WW
△	Influent	Direct discharge, organic WW
△		Direct discharge, organic and inorganic WW
△		Direct discharge, inorganic WW
Maximum values		
Symbol	**Type of value**	
−	80th percentile	
−	90th percentile	
−	Average values determined without removing abnormal discharges	
−	Highest monthly averages (i.e. smoothed out)	
✕	No information – probably real maximum (i.e. outliers not removed)	
−	Outliers removed	
−	Predefined maximum value	
−	Real maximum (i.e. outliers not removed)	

Concentrations given in the graphs showing both influent and effluent emissions are average values (mostly yearly averages), generally averages of 24-hour composite samples.

2.4.2   Sum parameters

2.4.2.1   COD, TOC and BOD

2.4.2.1.1   General

Substances which have an unfavourable influence on the oxygen balance are included in the indicative list of substances to be taken into account for fixing emission limit values in Annex II to the IED (2010/75/EU) [5, Directive 2010/75/EU 2010].

2.4.2.1.2   Chemical oxygen demand (COD)

COD is commonly used to indirectly measure the amount of organic compounds in water by measuring the mass of oxygen needed for their total oxidation to carbon dioxide. The most widespread COD monitoring methods use dichromate as an oxidising agent and mercury salts to suppress the influence of inorganic chloride. COD has to be considered in relation to total

suspended solids (TSS) since TSS removal efficiency affects performance achieved with respect to COD (see Section 2.4.2.2).

Care has to be taken when converting COD to TOC or vice versa using ratios; these ratios need to be well-established for each case. Theoretical COD/TOC ratios of organic substances range from 0.67 (oxalic acid) to 5.33 (methane). For those WWTPs where both COD and TOC data for the effluent were reported (33 out of a total of 95 directly discharging WWTPs), COD/TOC ratios range from 1.73 to 6.38 (median 3.0). Values higher than the theoretical range may be caused by measurement uncertainties or by the presence of oxidisable inorganic substances.

In Germany, for economic and environmental reasons, COD was replaced to some extent by TOC. A study conducted for the German Federal Environment Agency (UBA DE) on different industrial sectors showed that, for the chemical industry, the COD/TOC ratio was mostly in the range of 2.5–3.5 (median 2.9; 1 053 samples of 38 effluents) [97, Braun et al. 1999].

Overview of WWTP performance on COD
Out of a total of 95 directly discharging WWTPs, COD concentration values in the effluent were reported for 67 WWTPs (or 71 %), and for 48 (or 72 %) of the latter, COD values in the influent were also reported. Two effluent values were given as below a certain concentration (Figure 2.8 and Figure 2.9). Often 24-hour composite samples were taken on a daily basis.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
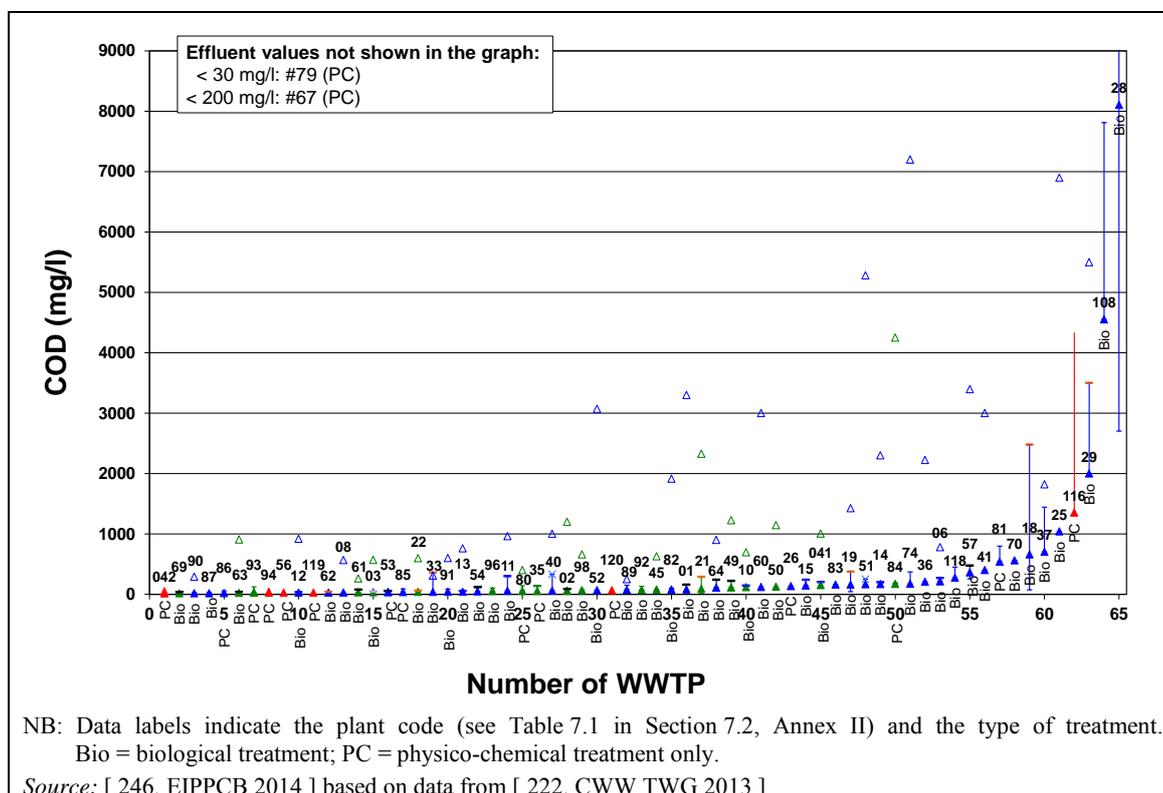
Figure 2.8: **Average COD concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (all WWTPs are shown)**

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; PC = physico-chemical treatment only.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
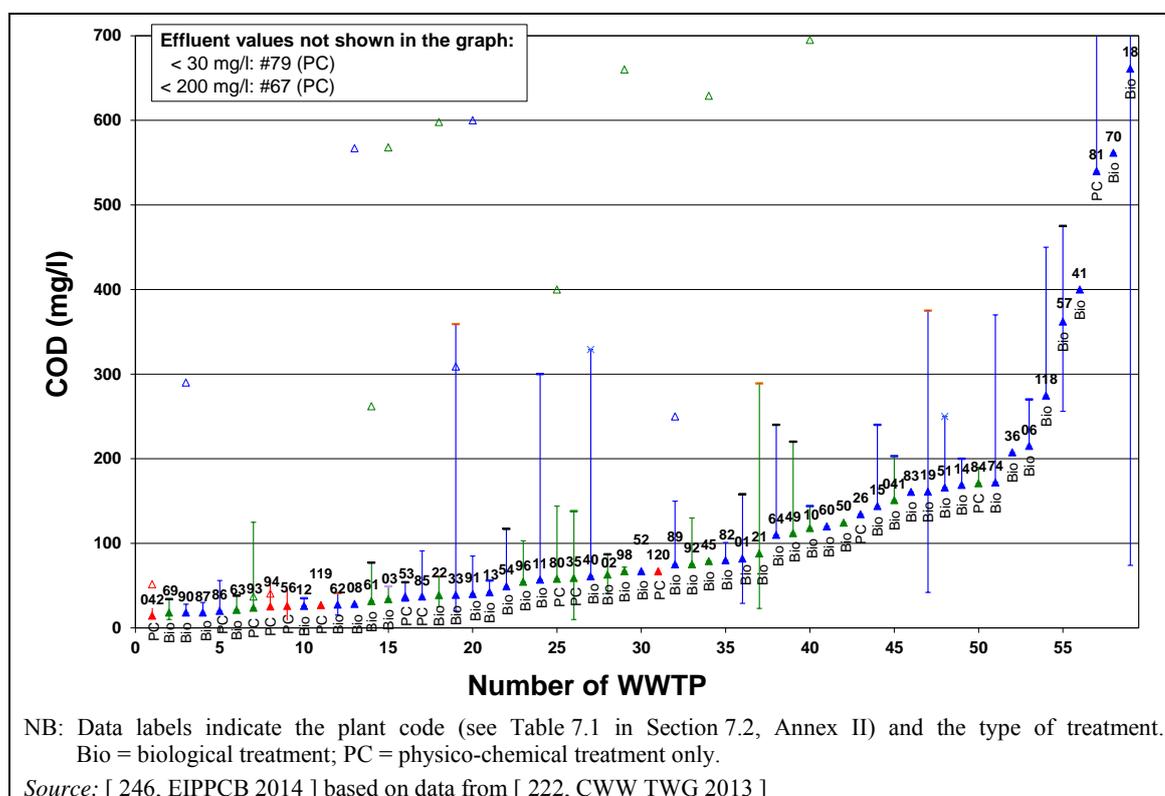
Figure 2.9: **Average COD concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (only WWTPs with effluent values ≤ 700 mg/l are shown)**

WWTPs showing either relatively high BOD_5 and/or TSS values in the effluent (e.g. #25, #28, #29, #37, #57, #108, #116) or WWTPs treating only waste waters from OFC plants (e.g. #06, #41, #70, #118) tend to have higher COD emissions.

Abatement efficiencies for loads reported for 44 WWTPs range from 4.1 % to 98.0 %, but more generally from 55.3 % to 97.0 % (10th to 90th percentile) with a median of 90.8 %. Efficiencies reported for loads and concentrations match in the vast majority of cases. Several installations achieve abatement efficiencies higher than 90 % with average effluent concentrations below 100 mg/l.

Techniques reported to reduce COD emissions
The following pretreatment operations (carried out at the installation(s) from which the waste waters originate) were reported in the questionnaires:

• stripping,
• distillation,
• adsorption,
• extraction,
• chemical oxidation,
• biological treatment,
• filtration.

Most of the installations with high COD concentrations in the influent to the final treatment (i.e. COD > 100 mg/l) use biological treatment (see Figure 2.8 and Figure 2.9). CMAS systems are most widely used for biological treatment (see Section 2.2).

Fluctuations of emissions around the average (in concentration)
Maximum COD values reported for 52 WWTPs vary around the average by a factor of 1.1–9.2, but more generally by a factor of 1.3–3.3 (10th to 90th percentile). Batch production or events such as shutdowns at the level of the individual chemical production plants can explain variations in COD emissions.

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), COD is considered not quantifiable below 7 mg O_2/l. In Spain, the limit of quantification for COD is 30 mg O_2/l. In Germany, the LOQ for COD is 15 mg O_2/l based on German standard DIN 38409–H 41–1. Two international standards for measuring COD exist. ISO 6060 (1989) is applicable to water with a value between 30 mg/l and 700 mg/l. The chloride content must not exceed 1 000 mg/l. If the value exceeds 700 mg/l, the water sample is diluted. For greatest accuracy, it is preferable that the value of the sample be in the range of 300–600 mg/l. ISO 15705 (2002) uses the sealed tube method which is applicable up to a COD value of 1 000 mg/l and a chloride concentration not exceeding 1 000 mg/l. The method has a limit of detection of 6 mg/l for photometric detection at 600 nm, and 15 mg/l for titrimetric detection. At low COD concentrations, measurements are prone to interference by high chloride levels. TOC measurements are much less sensitive in this respect.

Parameters that affect performance
Significant removal of the total organic loads depends mainly on the removal of the refractory organic fraction of this total load as well as on the optimum operation of the biological part of the treatment system to remove the biodegradable part.

Relevant refractory organic loading needs pretreatment or post-treatment depending on the concentration and the required effluent quality. Once the refractory organic loading has been taken care of, a number of parameters have to be kept under control to ensure the highest efficiency of the biological treatment (in terms of abatement/removal of pollutants, energy efficiency, production of sludge, odour nuisance, etc.). These parameters are, for the most part, specific to each type of biological treatment process used (suspended growth or fixed film processes) and to the technology chosen for the treatment process (e.g. trickling filter, sequencing batch reactor, membrane bioreactor). However, as a rule of thumb, smooth operation, especially with limited variations of loads and characteristics of the influent waste water, is generally desirable, especially for activated sludge processes. One should also bear in mind that (seasonal) ambient temperatures as well as the waste water temperature affect the biological treatment.

Biological treatment takes time (days to weeks) to recover from upset conditions (sudden variations in the flow and load). In extreme conditions the whole population of bacteria/microorganisms has to be replaced. Fixed biomass could be less sensitive to upset conditions.

Excessive amounts of spent caustic (used for example to abate SO_X emissions) can quickly overwhelm a waste water treatment system due to the normally high COD of the spent caustic. Another issue can be a significant increase in ammonium and sulphide loads that result from upsets in the operation of strippers. These loads can, in turn, upset a biological treatment system if it is not designed to handle ammonium and sulphide.

Restrictions on water usage or high levels of water recycling can explain the relatively high concentration of COD (and of pollutants in general) even if high abatement efficiency is achieved.

Relationship between performance and techniques used, as reported in the questionnaires
There is no clear performance trend associated with the use of certain technologies or combinations thereof. The final effluent concentration very much depends on the way the WWTP is designed, maintained, and operated. A large panel of techniques allows for achieving

COD discharges below the 50th percentile for COD (i.e. approximately 100 mg/l as a yearly average of 24-hour composite samples).

Regardless of the type of treatment system selected, one of the keys to effective biological treatment is to develop and maintain an acclimated, healthy biomass, sufficient in quantity to handle maximum flows and the organic loads to be treated.

2.4.2.1.3   Total organic carbon (TOC)

Total organic carbon (TOC) analysis is used to directly measure the amount of organic compounds in water. The most widespread methods use a combustion chamber to completely oxidise the organic substances to carbon dioxide which is then measured by spectrometry. Inorganic carbon is not included in the TOC. Identifying changes in the normal/expected TOC concentrations can be a good indicator of potential threats to a waste water treatment system. Various online TOC analysers exist. There is a trend to replace COD with TOC for economic and ecological reasons.

Overview of WWTP performance on TOC
Out of a total of 95 directly discharging WWTPs, TOC concentration values in the effluent were reported for 45 WWTPs (or 47 %), and for 22 (or 49 %) of the latter, TOC values in the influent were also reported (Figure 2.10 and Figure 2.11). Often 24-hour composite samples were taken on a daily, weekly or semi-monthly basis.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
    Bio = biological treatment; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
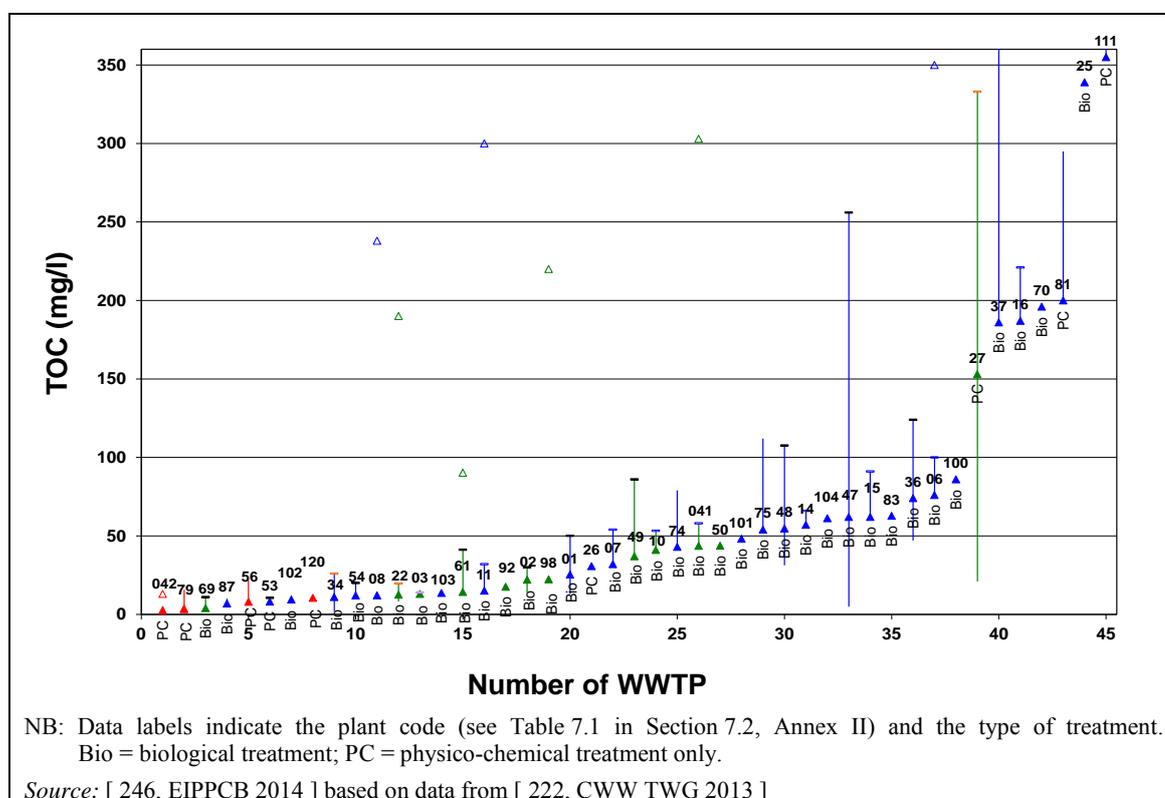
Figure 2.10: Average TOC concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (all WWTPs are shown)
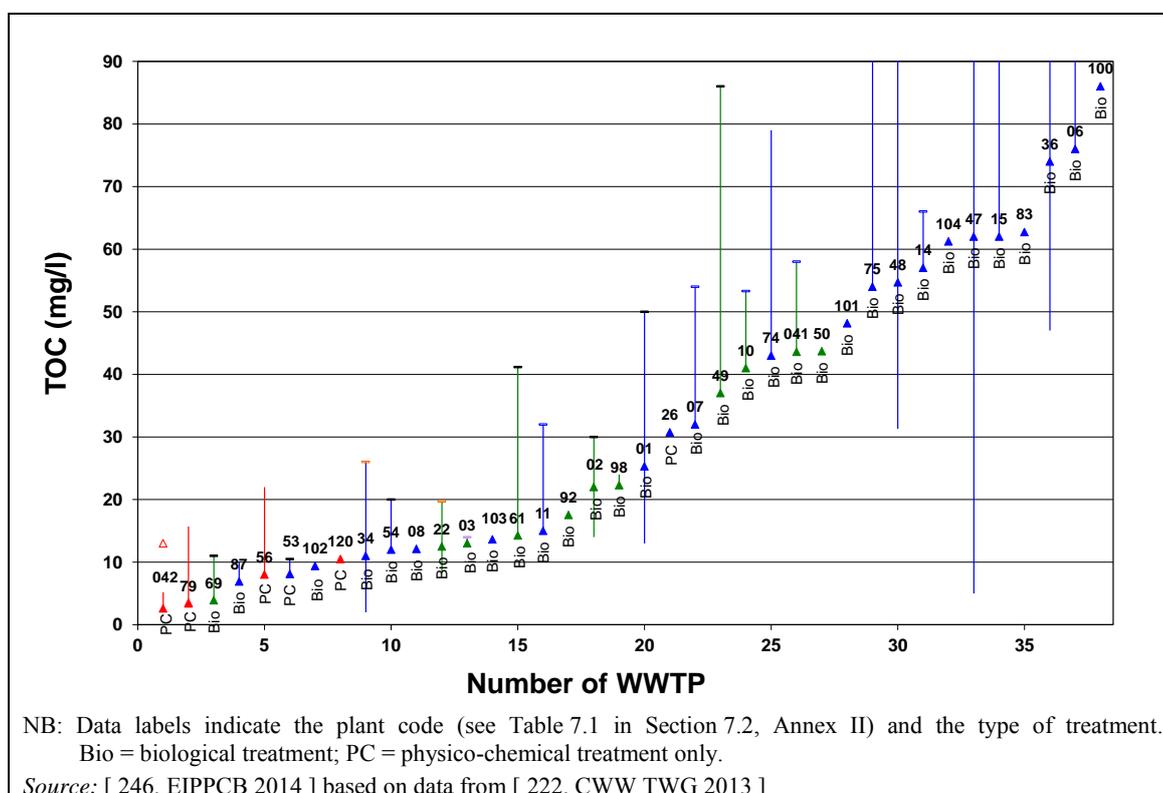
Figure 2.11: Average TOC concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (only WWTPs with effluent values ≤ 90 mg/l are shown)

Abatement efficiencies for loads reported for 19 WWTPs range from 4.1 % to 97.7 %, but more generally from 78.3 % to 96.9 % (10th to 90th percentile) with a median of 91.4 %.TOC abatement efficiencies are similar to COD abatement efficiencies.

Techniques reported to reduce TOC emissions
The techniques are the same as those indicated under the COD section (see Section 2.4.2.1.2).

Fluctuations of emissions around the average (in concentration)
Maximum TOC values reported for 29 WWTPs vary around the average by a factor of 1.1–4.7, but more generally by a factor of 1.2–2.9 (10th to 90th percentile). COD and TOC fluctuations are similar.

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), TOC is considered not quantifiable below 10 mg/l. The international standards for measuring TOC are EN 1484 (1997) and ISO 8245 (1999). Both standards are guidelines to measure TOC by oxidation via combustion, addition of an appropriate oxidant, UV radiation, or any other high-energy radiation. The carbon dioxide formed is determined either directly or after reduction while the final determination of carbon dioxide is carried out by a number of different procedures, for example: infrared spectrophotometry, titration, thermal conductivity, conductometry, coulometry, use of carbon dioxide-sensitive sensors and flame ionisation detection. Inorganic carbon is removed by acidification and purging, or is determined separately. EN 1484 gives an application range of 0.3–1 000 mg/l while the lower value is only applicable in special cases, for example drinking water, measured with instruments capable of measuring these low levels.

Parameters that affect performance
See discussion under the COD parameter (see Section 2.4.2.1.2).

Relationship between performance and techniques used as reported in the questionnaires
See discussion under the COD parameter (see Section 2.4.2.1.2).

2.4.2.1.4   Biochemical oxygen demand after five days (BOD$_5$)

BOD$_5$ measures the amount of dissolved oxygen required or consumed after five days at a constant temperature for the microbiological decomposition (oxidation) of organic material in water.

The concentration in the effluent is generally a more pertinent parameter than the abatement efficiency.

The parameters COD and TOC are faster to determine than BOD$_5$. Furthermore, the use of BOD$_5$ as a parameter to describe the efficiency of biological treatment has some disadvantages such as:

- the monitoring method used is not very accurate considering reproducibility and methodology dependence (dilution method versus respirometer for example);
- the analytical result depends on the local conditions of the laboratory, such as the inoculum used for the test;
- the BOD$_5$ measurement does not allow for any prediction on the performance within the WWTP; it only provides an indication as to whether the waste water is easily degradable to a certain rate.

The ratio BOD$_5$/COD in the raw effluent cannot be used as an operational parameter for the waste water treatment, but gives a rough indication of biodegradability. As a rule of thumb, BOD$_5$/COD ratios before treatment of < 0.2 indicate relatively non-degradable organic substances, ratios between 0.2 and 0.4 indicate moderately to highly degradable organic substances, and ratios of > 0.4 indicate highly degradable organic substances (see Section 3.3.2.3.5). More than 90 % of the WWTPs surveyed treat waste waters with BOD$_5$/COD ratios of > 0.2, i.e. waste waters with presumably moderately to highly degradable organic substances. In the effluents, the BOD$_5$/COD ratios are mostly < 0.2, indicating waste waters with relatively non-degradable substances.

Overview of WWTP performance on BOD$_5$
Out of a total of 95 directly discharging WWTPs, BOD$_5$ concentration values in the effluent were reported for 58 WWTPs (or 61 %), and for 36 (or 62 %) of the latter, BOD$_5$ values in the influent were also reported. Six effluent values were given as below a certain concentration or below the limit of detection (Figure 2.12 and Figure 2.13). Often 24-hour composite samples were taken on a daily, weekly or semi-monthly basis.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
Bio = biological treatment; LOD = limit of detection; PC = physico-chemical treatment only.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
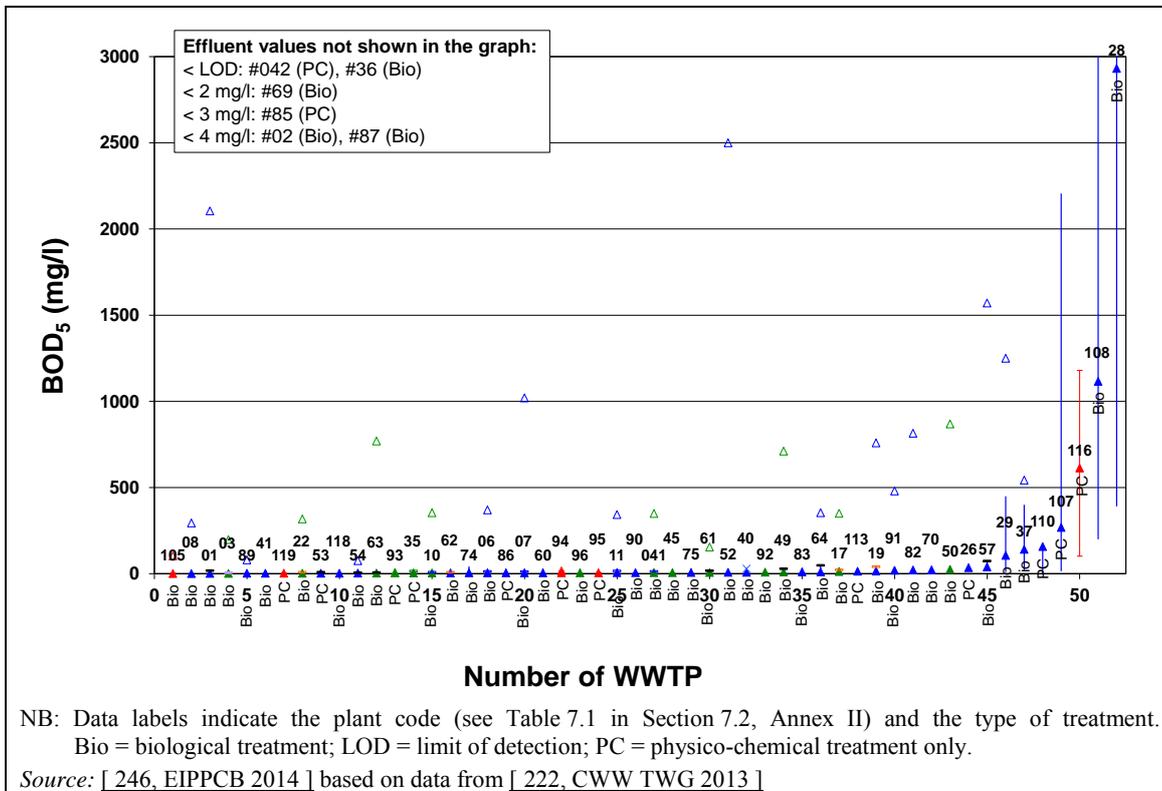
Figure 2.12: Average BOD₅ concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (all WWTPs are shown)

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
Bio = biological treatment; LOD = limit of detection; PC = physico-chemical treatment only.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
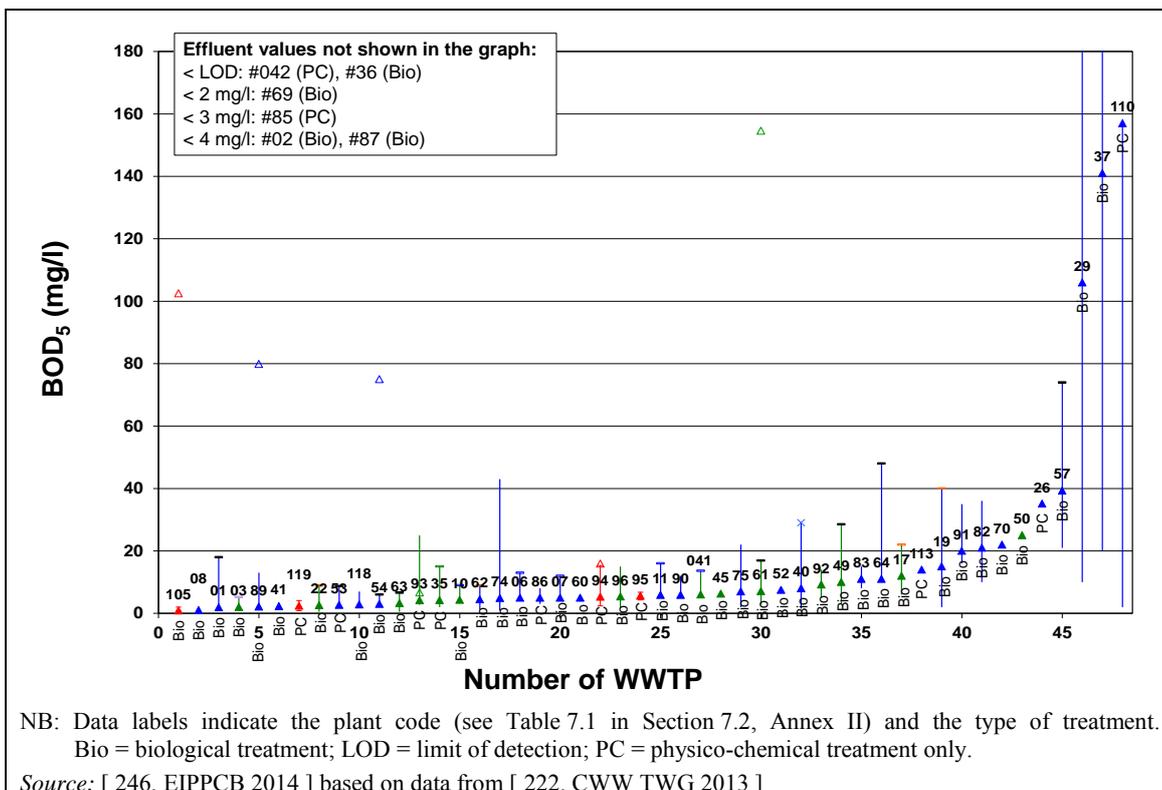
Figure 2.13: Average BOD₅ concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (only WWTPs with effluent values ≤ 180 mg/l are shown)

Abatement efficiencies for loads reported for 33 WWTPs range from 37.8 % to 99.96 %, but more generally from 78.1 % to 99.7 % (10th to 90th percentile) with a median of 97.9 %. Efficiencies reported for loads and concentrations match in the vast majority of the cases.

Techniques reported to reduce BOD_5 emissions
The techniques used to remove COD (see Section 2.4.2.1.2) may remove (part of the) BOD_5 too; on the other hand, pretreatment of COD may in certain cases raise BOD_5 (conversion of non-degradable to biodegradable matter, e.g. by partial oxidation). The only technique which is *a priori* dedicated to removing BOD_5 is biological treatment.

Fluctuations of emissions around the average (in concentration)
Maximum BOD_5 values reported for 43 WWTPs vary around the average by a factor of 1.2–9.5, but more generally by a factor of 1.6–5.3 (10th to 90th percentile). BOD_5 fluctuations are slightly higher than COD and TOC fluctuations.

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), BOD_5 is considered not quantifiable below 3 mg O_2/l. In Spain, the LOQ for BOD_5 is 8 mg O_2/l. In Sweden, BOD_7 is monitored instead of BOD_5. Four international standards for measuring BOD exist. EN 1899–1 (1998) and ISO 5815–1 (2003) specify a BOD determination of waters by dilution and seeding with suppression of nitrification by allylthiourea. They are applicable to all waters with biochemical oxygen demands greater than or equal to 3 mg/l of oxygen (the limit of quantification) and not exceeding 6 000 mg/l of oxygen. EN 1899–2 (1998) and ISO 5815–2 (2003) specify a BOD determination of undiluted waters samples. They are applicable to BOD values greater than or equal to 0.5 mg/l of oxygen (the limit of quantification) and not exceeding 6 mg/l of oxygen.

Parameters that affect performance
See discussion on biological treatment under the COD parameter (see Section 2.4.2.1.2).

Since $BOD_5 <$ COD, the monitoring of BOD_5 is not essential when COD or TOC is low.

Relationship between performance and techniques used as reported in the questionnaires
See discussion under the COD parameter (see Section 2.4.2.1.2). One Member State mentioned that it can be expected that BOD_5 concentrations in the effluent/performance are less dependent on the variation of the production than COD/TOC, and can be controlled by the proper operation of the final treatment alone.

2.4.2.2   Total suspended solids (TSS)

Materials in suspension are included in the indicative list of substances to be taken into account for fixing emission limit values in Annex II to the IED (2010/75/EU) [5, Directive 2010/75/EU 2010].

There are some reasons to link the analysis of TSS with other parameters. If BOD/COD/TOC removal functions poorly, TSS emissions may be affected. Conversely, high TSS values can correlate with/cause high concentrations of other parameters, namely BOD, COD/TOC, total phosphorus, total nitrogen, and metals.

It is possible to have higher TSS values in the effluent than in the influent, for example due to the growth of biomass during biological treatment or due to the precipitation of compounds during physico-chemical treatment. In most cases, it therefore does not make sense to calculate abatement efficiencies for the WWTP.

Overview of WWTP performance on TSS
Out of a total of 95 directly discharging WWTPs, TSS values in the effluent were reported for 76 WWTPs (or 80 %). Two effluent values were given as below a certain concentration or below the limit of detection (Figure 2.14, Figure 2.15, and Figure 2.16). Often 24-hour composite samples were taken on a daily basis.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; Filtr = filtration; Flot = flotation; LOD = limit of detection; NI = no information provided; NT = no final treatment; PC = physico-chemical treatment only; SF = sand filtration; Sed = sedimentation; Ultraf = ultrafiltration.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
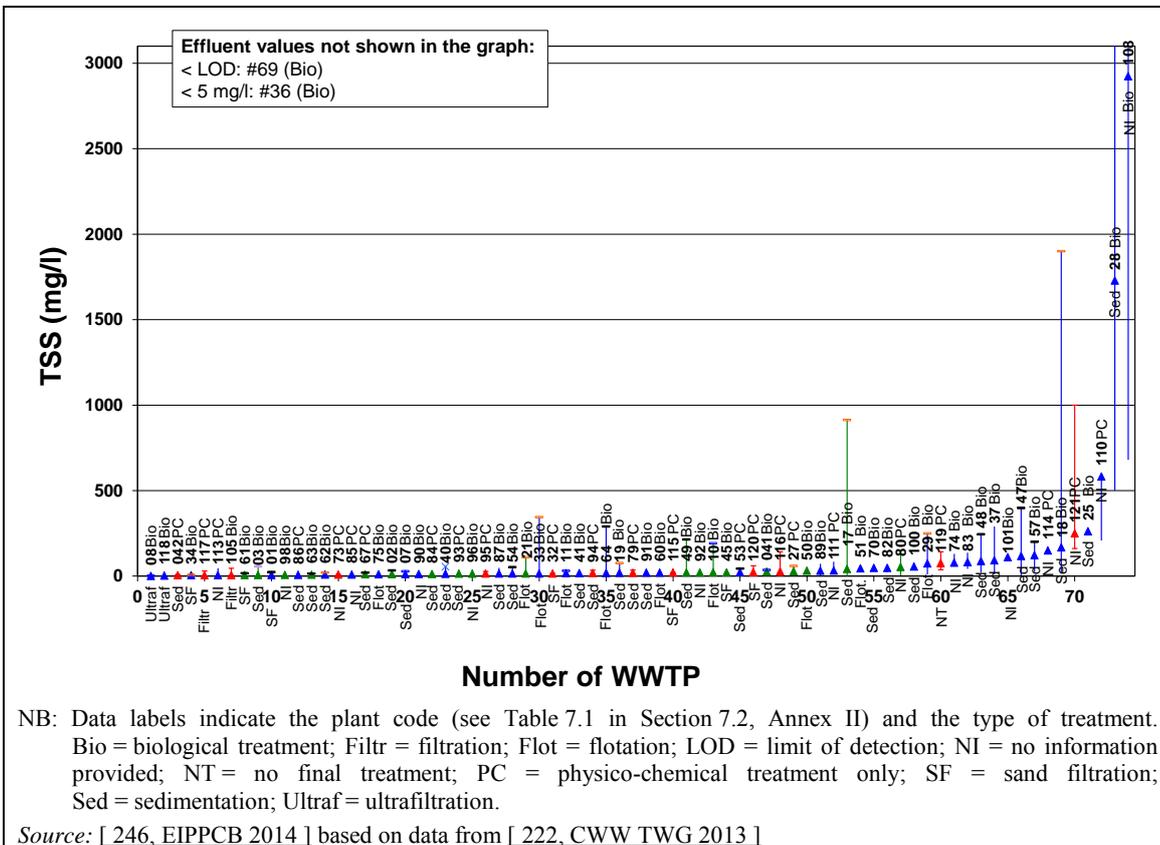
Figure 2.14: Average TSS concentrations (mostly yearly averages) in the effluents of directly discharging WWTPs (all WWTPs are shown)

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; Filtr = filtration; Flot = flotation; LOD = limit of detection; NI = no information provided; NT = no final treatment; PC = physico-chemical treatment only; SF = sand filtration; Sed = sedimentation; Ultraf = ultrafiltration.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
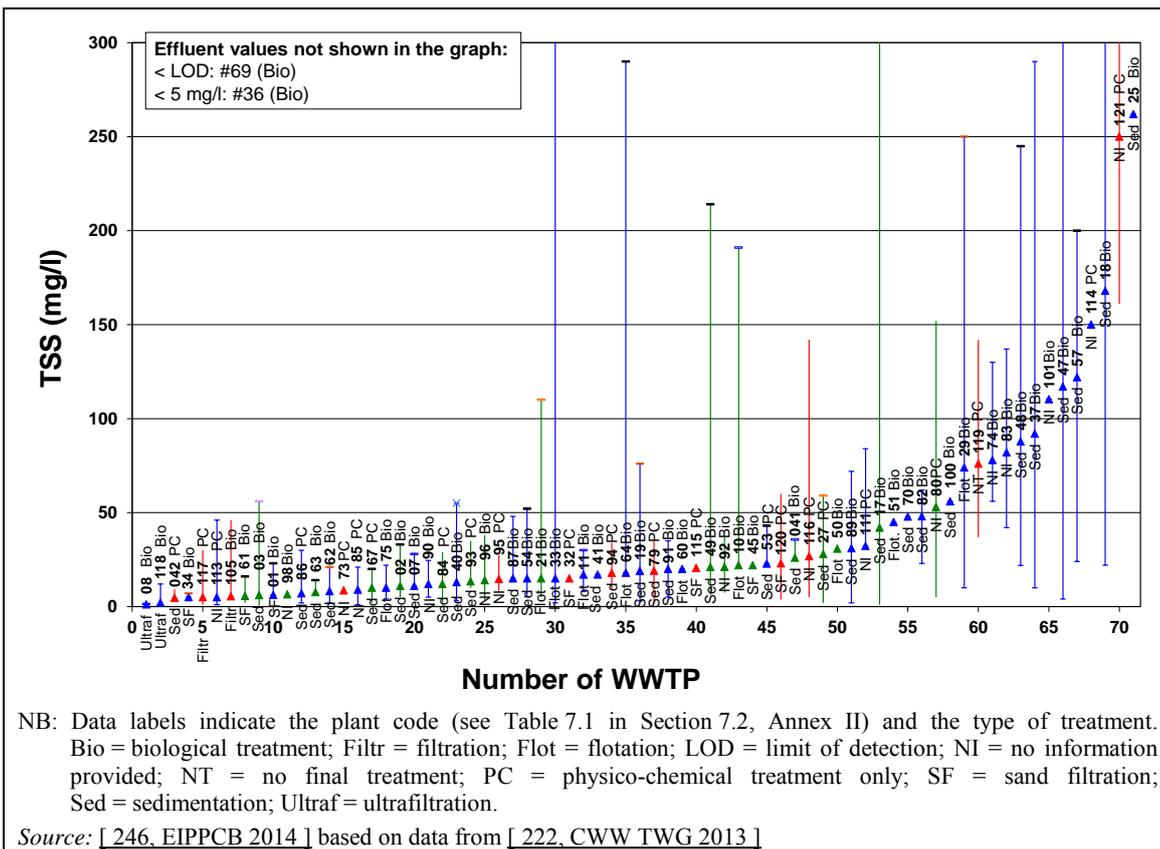
Figure 2.15: Average TSS concentrations (mostly yearly averages) in the effluents of directly discharging WWTPs (only WWTPs with effluent values ≤ 300 mg/l are shown)

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
Bio = biological treatment; Filtr = filtration; Flot = flotation; LOD = limit of detection; NI = no information provided; NT = no final treatment; PC = physico-chemical treatment only; SF = sand filtration; Sed = sedimentation; Ultraf = ultrafiltration.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]

Figure 2.16: Average TSS concentrations (mostly yearly averages) in the effluents of directly discharging WWTPs (only WWTPs with effluent values ≤ 50 mg/l are shown)

WWTPs showing either relatively high BOD_5 and/or COD/TOC values in the effluent (e.g. #18, #25, #28, #57, #108, #110) tend to have higher TSS emissions.

Techniques reported to reduce TSS emissions
The techniques used for final solids removal are given in Section 2.2, as well as in Figure 2.14, Figure 2.15, and Figure 2.16. Sedimentation is most widely used, followed by flotation. Filtration and flotation are often preceded by a sedimentation step.

Fluctuations of emissions around the average (in concentration)
Maximum TSS values reported for 58 WWTPs vary around the average by a factor of 1.3–23, but more generally by a factor of 1.6–9.2 (10th to 90th percentile). TSS fluctuations are significantly higher than COD and TOC fluctuations. Seasonal variations (e.g. rain season) and the treatment of storm water (sometimes from a nearby city) may cause higher variability in the TSS effluent concentration.

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), TSS is considered not quantifiable below 2 mg/l. In Spain, the LOQ for TSS is 2 mg/l. Two international standards, EN 872 (2005) and ISO 11923 (1997), describe a method for the determination of suspended solids in raw waters and waste waters by filtration though glass fibre filters. The lower limit of the determination is in both cases approximately 2 mg/l.

Parameters that affect performance
The performance of the techniques used for final solids removal is influenced by the characteristics (e.g. settleability) and concentration of the suspended solids. Biological WWTPs with high influent loads of BOD_5 (e.g. some OFC plants) generally generate more biomass during treatment and therefore will require more sophisticated techniques to achieve the same TSS emission level as a biological WWTP with lower influent loads of BOD_5.

Relationship between performance and techniques used as reported in the questionnaires
The performance of the WWTPs with respect to the removal of solids depends on the techniques used, but also on the characteristics of the waste waters and the operating conditions of the installations (e.g. residence time in the final clarifier in the case of sedimentation).

Average TSS values below 25 mg/l are achieved by WWTPs using sand filtration (e.g. #34: 5 mg/l, #01: 6 mg/l, #61: 6 mg/l, #32: 15 mg/l, #115: 21 mg/l, #45: 22 mg/l, and #120: 23 mg/l). Installations using ultrafiltration as the main solids removal step (often as part of a membrane bioreactor) show very low TSS values in the effluent (i.e. #36: < limit of detection, #08: 1 mg/l, #118: 2 mg/l, and #69: < 5 mg/l). In the case of the installations #41 and #70, only part of the effluent is treated by the membranes, and therefore TSS emissions are higher (17 mg/l and 48 mg/l, respectively).

Directly discharging WWTPs using flotation tend to show higher TSS values in the effluent (15–120 mg/l), although nine out of the eleven WWTPs reporting the use of flotation achieve average TSS values below 35 mg/l (i.e. #10, #11, #21, #33, #35, #50, #60, #64, #75) and five of them even below 20 mg/l (i.e. #11, #21, #33, #64, and #75). The largest spread of TSS effluent values is found when sedimentation as the main solids removal step is used (5–2 900 mg/l). Nevertheless, among the 34 directly discharging WWTPs using sedimentation and reporting TSS emission values, 17 WWTPs achieve average TSS values below 20 mg/l, and 23 WWTPs achieve average TSS values below 35 mg/l.

2.4.2.3 Adsorbable organically bound halogens (AOX)

AOX is a sum parameter which indicates the overall level of organohalogen compounds (chlorine, bromine and iodine) in water samples. It is important as many organohalogen compounds are toxic (especially the fat-soluble chlorinated group – dioxins, furans, and polychlorinated phenolic compounds) and/or persistent. However, as a sum parameter, AOX does not give information on the chemical structure of organohalogen compounds present or on their toxicity. The AOX method has the advantage that it is quite a simple measurement if it is compared with the alternative methods of measuring levels of individual compounds which are complex and require costly equipment. High concentrations of organic compounds or chloride may interfere with the AOX measurement. AOX is an operational parameter, i.e. the measurement procedure determines the result. AOX cannot be used to monitor very volatile compounds. AOX is mainly associated with the production of organic chemicals and silicones.

EOX (extractable organically bound halogens) is a sum parameter that can be used as an alternative to AOX. EOX only covers non-polar organic compounds, and therefore AOX values are generally higher than EOX values.

AOX has been routinely monitored in Germany since the 1980s, but less so in Austria, Belgium, the Czech Republic, France, Italy, the Netherlands, Poland, Spain, and Sweden. EOX monitoring is used in Belgium, France and the Netherlands.

Waste water streams containing high AOX loads are preferably pretreated or recovered separately, e.g. by (chemical) oxidation, adsorption, filtration, extraction, (steam) stripping, hydrolysis (to improve biodegradability), distillation, membrane processes or anaerobic pretreatment.

Overview of WWTP performance on AOX
Out of a total of 95 directly discharging WWTPs, AOX concentration values in the effluent were reported for 42 WWTPs (or 44 %), and for 15 (or 36 %) of the latter, AOX values in the influent were also reported. One effluent value was given as below the limit of detection (Figure 2.17 and Figure 2.18). A few plants reported EOX values or measurements of individual halogenated organic compounds via gas chromatography. Often 24-hour composite samples were taken on a daily, weekly or semi-monthly basis.
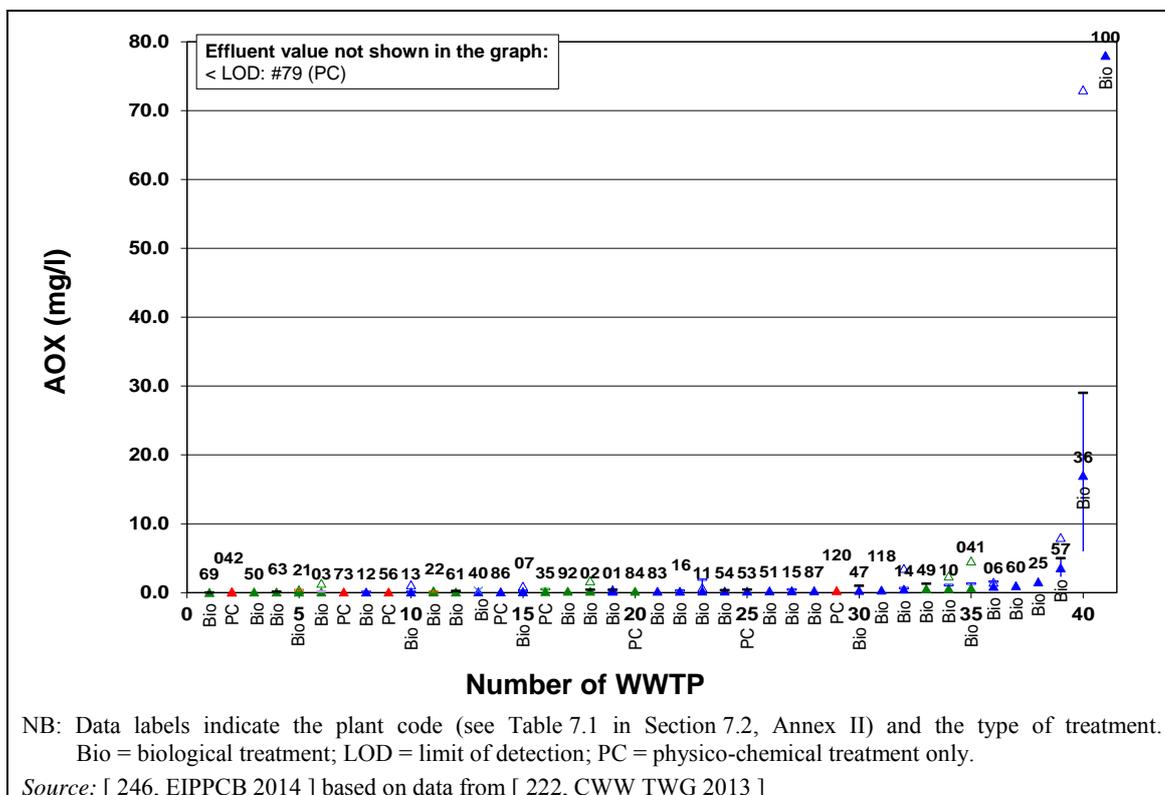
Figure 2.17: Average AOX concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (all WWTPs are shown)
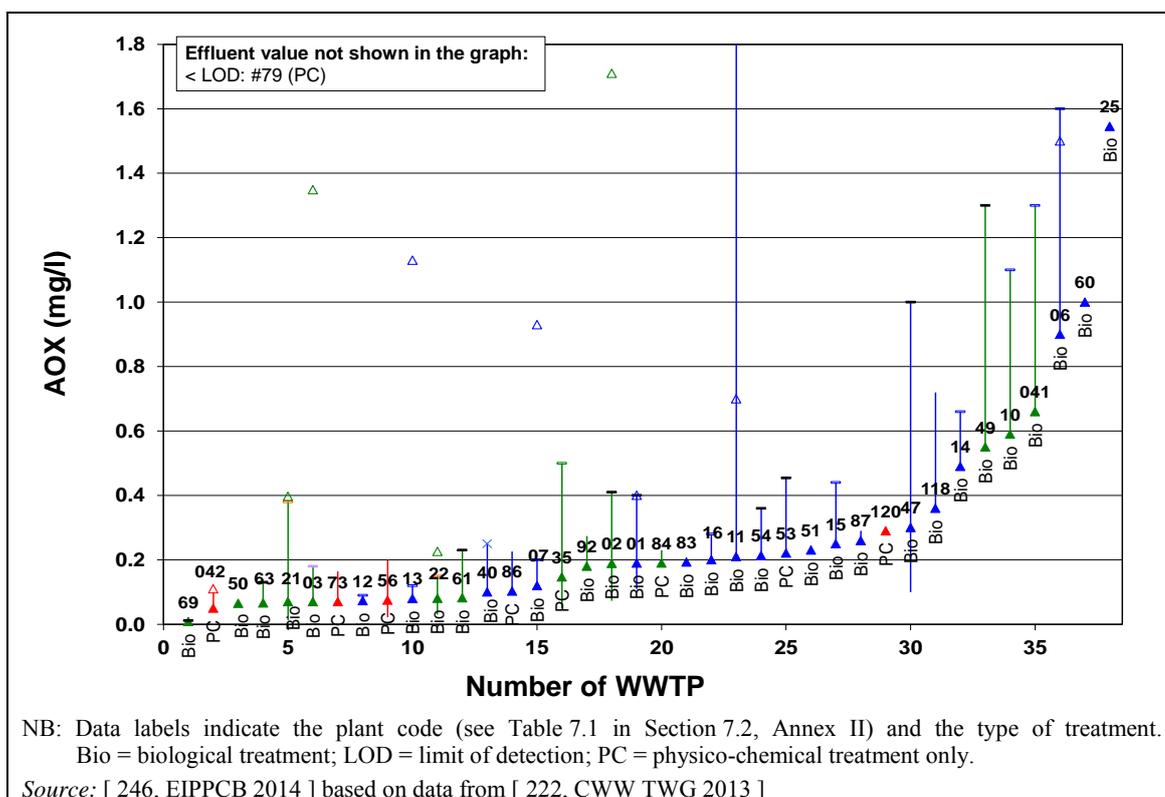
Figure 2.18: Average AOX concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (only WWTPs with effluent values ≤ 1.8 mg/l are shown)

Average AOX levels in the effluents are generally < 1 mg/l. At four WWTPs (i.e. #100 with 78 mg/l, #36 with 17 mg/l, #57 with 3.6 mg/l, and #25 with 1.6 mg/l), AOX emission levels are > 1 mg/l. Installation #36 produces iodinated X-ray contrast agents and installation #06 organic fine chemicals (e.g. optical brighteners, dyes, antimicrobial chemicals). Bleach is used as an oxidising agent during pretreatment at installation #57.

Techniques reported to reduce AOX emissions
The main techniques to reduce AOX emissions are the segregation and selective pretreatment of waste water streams from processes where AOX is an issue.

The following pretreatment techniques (carried out at the installation(s) from which the waste waters originate) were reported in the questionnaires:

- oxidation (i.e. #07),
- stripping (i.e. #12, #14, #15, #17, #19, #21, #22, #36),
- adsorption on activated carbon (i.e. #13, #15, #21),
- decantation (i.e. #17),
- oil-water separation (i.e. #27),
- distillation (i.e. #36).

Regarding AOX removal at the WWTPs, the following techniques were reported:

- stripping (i.e. #27),
- adsorption on activated carbon (i.e. #07, #34).

A certain share of the AOX is also removed during final treatment (e.g. due to biodegradation or due to adsorption to particles).

Fluctuations of emissions around the average (in concentration)
Maximum AOX values reported for 31 WWTPs vary around the average by a factor of 1.1–9.0, but more generally by a factor of 1.4–3.2 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), AOX is considered not quantifiable below 20 µg/l. In Germany, the LOQ for AOX is 15 µg/l. The most widely accepted monitoring method is EN ISO 9562 (2004) which replaced the European standard EN 1485 (1997). The standard specifies a method for the direct determination of an amount of usually 10 µg/l in water of organically bound chlorine, bromine and iodine (expressed as chloride) adsorbable on activated carbon. This method is applicable to test samples with concentrations of inorganic chloride ions of less than 1 g/l. Samples with higher concentrations are diluted prior to analysis.

No European or international standard for the determination of EOX exists. The standards for the determination of EOX are DIN 38408–H8 (1984) in Germany, NEN 6402 (1991) in Flanders (Belgium), and OENORM M 6614 in Austria. In Flanders (Belgium), the LOQ for EOX is 5 µg Cl/l.

Parameters that affect performance
Organohalogen compounds are part of the organic load of waste waters. AOX is therefore a part of COD/TOC, and, if biodegradable, also of BOD_5. See therefore the discussion under the COD parameter in Section 2.4.2.1.2.

Relationship between performance and techniques used as reported in the questionnaires
See the discussion under the COD parameter in Section 2.4.2.1.2.

2.4.3 Metals

2.4.3.1 General

Important characteristics of (heavy) metals which influence waste water treatment are given below:

- metals are not degradable and almost all of them are adsorbed to the sludge or passed through the biological WWTP;
- high levels of metals can inhibit the biological processes in WWTPs, but certain concentrations are needed for the growth of the organisms;
- high metal loadings in waste water sludge cause problems for disposal (in the case of agricultural use of waste water sludge);
- organic compounds (especially those containing nitrogen such as EDTA) may act as chelates and keep (heavy) metals in solution and can even release already precipitated metals;
- once discharged to water, metals from sediment can remobilise in the water body (river or sea).

The waste waters of many chemical processes contain metals, e.g. they are contained in the materials used for chemical processing (feedstock, auxiliaries and catalysts). The corrosion of pipes and equipment is also an important source of metals (especially Cu, Cr, Ni, Zn) in effluents of WWTPs (in low concentrations, however often representing the main input regarding loads).

Metals are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Averaging periods used for reporting emissions
Sampling frequency varies considerably, from once per day to once per year. Mostly grab samples or composite samples over a short duration (2–24 h) were taken. Averaging periods are on a yearly basis.

Techniques reported to reduce metal emissions
The main techniques to reduce emissions of metals are the segregation and selective pretreatment of waste water streams from processes where metals are an issue. During biological treatment of waste water, metals can be removed by biomass as a positive side effect either through an active uptake (bioaccumulation) or by passive biosorption. The extent to which metals are removed depends on several factors, for example pH, nature and concentration of biomass and inorganic particles, and the chemical state of the metal ion (oxidation state, complexation).

Parameters that affect performance
The removal of metals is a positive side effect of biological waste water treatment. Increasing the concentration of biomass during treatment and reducing solids in the effluent increases the transfer of metals to the sludge and thus increases their removal. This is especially true for those metals which tend to be bound to particles.

Organometallic compounds may be more difficult to remove from waste waters (this depends on the compounds and the waste water composition). Under unfavourable conditions, the achievable elimination may be lower and/or the treatment more difficult/expensive.

Relationship between performance and techniques used as reported in the questionnaires
In many cases, high removal efficiencies are achieved by the WWTPs and special pretreatment is only used for selected tributary streams.

Given that the removal of metals is a positive side effect and that applied techniques are heterogeneous combinations of basic operations, no relationship between performance and specific techniques could be established.

Limits of detection (LOD) and quantification (LOQ)
Limits of detection and quantification depend on the analytical method, the instruments and the reagents used, but also on the presence of interfering constituents (matrix). Lower limits of application (LLA) and LODs/LOQs are described in European (CEN) and International standards (ISO) but are sometimes outdated.

2.4.3.2   Cadmium (Cd)

Although cadmium is usually not expected at the outlet of the WWTPs, it can sometimes be found as a contaminant, e.g. in the effluent of phosphate production (cadmium is found as a trace element in phosphate rock), or when catalysts are used in production. Cadmium emissions at sites which do not use cadmium in their processes are expected to be below the limit of quantification (i.e. < 2 µg/l).

Cadmium is included in the list of priority hazardous substances in Annex X to the Water Framework Directive [28, Directive 2000/60/EC 2000]. Substances of this annex are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Overview of WWTP performance on Cd
Out of a total of 95 directly discharging WWTPs, Cd concentration values in the effluent were reported for 48 WWTPs (or 51 %), and for 10 (or 21 %) of the latter, Cd values in the influent were also reported. Some 18 effluent values were given as below a certain concentration or below the limit of detection (Figure 2.19).

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; LOD = limit of detection; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
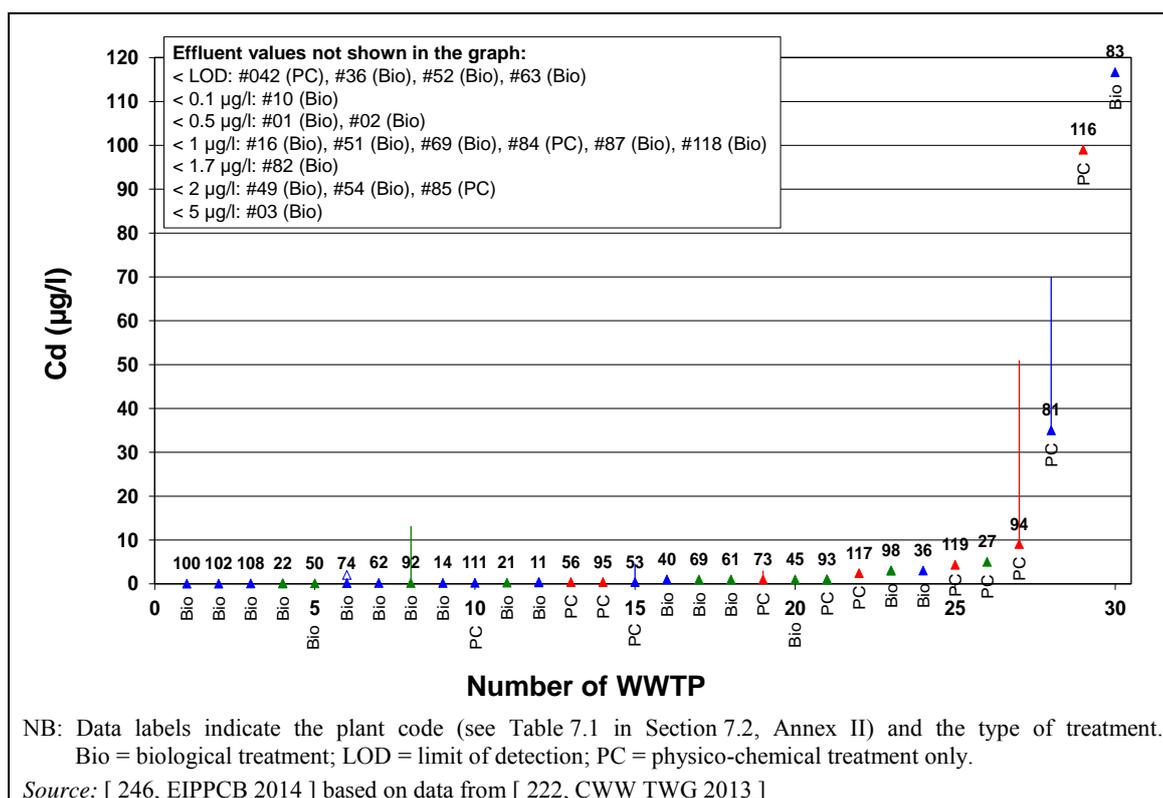
Figure 2.19:   Average Cd concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs

Average Cd levels in the effluents are generally ≤ 1 µg/l. Effluent concentrations > 1 µg/l were reported for the WWTPs #27, #36, #81, #83, #94, #98, #116, #117, and #119. Installation #94 produces fertilisers. The WWTPs #27, #81, #83, #116, and #117 also showed high emission levels of other metals, while the WWTPs #83 and #119 also showed high emission levels of TSS (i.e. > 35 mg/l).

Techniques reported to reduce Cd emissions
The following pretreatment and treatment techniques (carried out at the installation(s) from which the waste waters originate or the final WWTP) were reported in the questionnaires:

- precipitation and filtration (with other metals),
- ion exchange (with other metals).

Fluctuations of emissions around the average (in concentration)
Maximum Cd values reported for 19 WWTPs vary around the average by a factor of 1.0–66, but more generally by a factor of 1.0–6.8 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium) as well as in France, Cd is considered not quantifiable below 2 µg/l. In Germany, the LOQ for Cd is 0.01 µg/l based on EN ISO 17294–1. Analytical methods to measure Cd include inductively coupled plasma-optical emission spectrometry (ICP-OES) with an approximate LOQ of 0.2 µg/l (EN ISO 11885) and inductively coupled plasma-mass spectrometry (ICP-MS) with a lower limit of application of approximately 0.1 µg/l (EN ISO 17294–1).

2.4.3.3   Chromium total (total-Cr)

The corrosion of pipes and equipment is an important source of chromium in the influent of WWTPs. At some sites, the manufacture of organic chromium compounds (e.g. dyes) is a source of chromium in waste waters.

Overview of WWTP performance on total-Cr
Out of a total of 95 directly discharging WWTPs, total-Cr concentration values in the effluent were reported for 53 WWTPs (or 55 %), and for 12 (or 23 %) of the latter, total-Cr values in the influent were also reported. Some 16 effluent values were given as below a certain concentration or below the limit of detection (Figure 2.20).
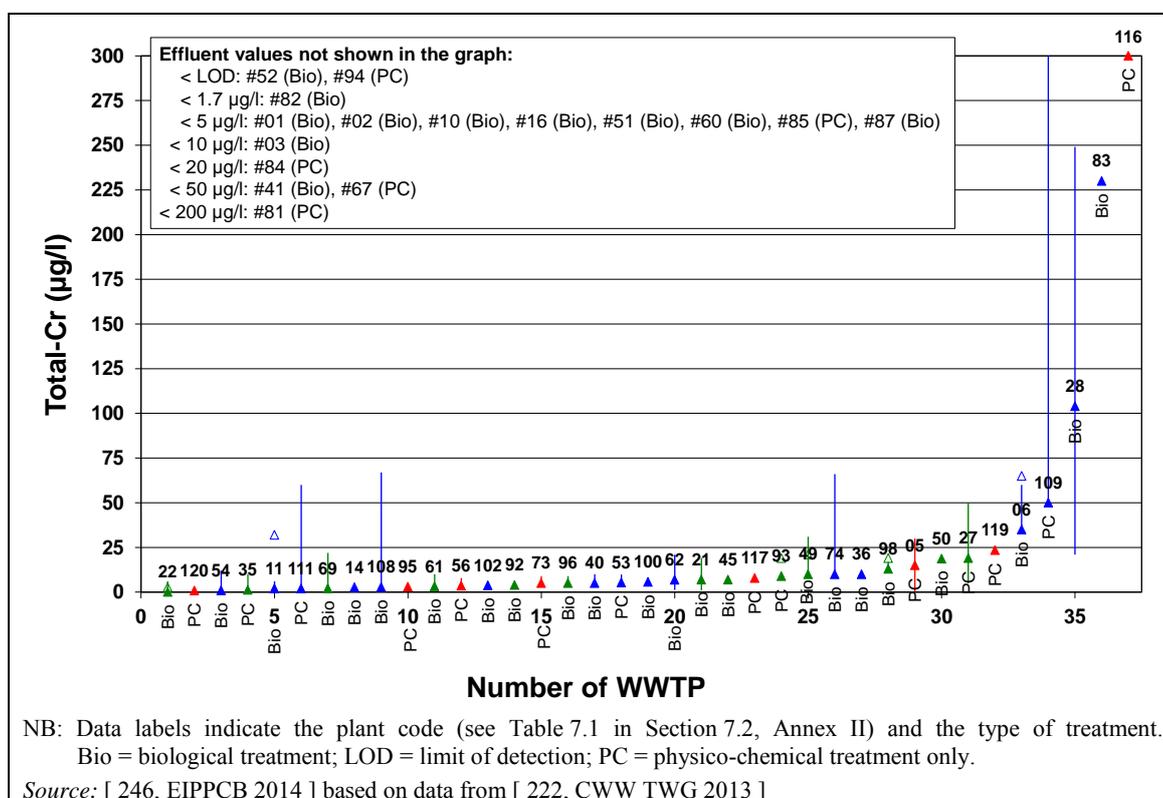
Figure 2.20: Average total-Cr concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs

Average total-Cr levels in the effluents are generally ≤ 25 µg/l. Effluent concentrations > 25 µg/l were reported for the WWTPs #06, #28, #83, #109, and #116. Installation #06 produces chromium-organic dyes. The WWTPs #28, #83, and #116 also showed high emission levels of other metals, while the effluents of the WWTPs #28 and #83 also showed high emission levels of TSS (i.e. > 35 mg/l).

Total-Cr can often be effectively abated by biological treatment; this is shown by WWTPs #02, #11, and #22 (abatement efficiency > 90 %). However, in the case of WWTP #06, the abatement efficiency is < 50 % due to the presence of chromium-organic compounds.

Techniques reported to reduce total-Cr emissions
The following pretreatment and treatment operations (carried out at the installation(s) from which the waste waters originate or the final WWTP) were reported in the questionnaires:

- precipitation and filtration (with other metals),
- ion exchange (with other metals),
- activated sludge systems.

Fluctuations of emissions around the average (in concentration)
Maximum total-Cr values reported for 24 WWTPs vary around the average by a factor of 1.0–76, but more generally by a factor of 1.4–20 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), total-Cr is considered not quantifiable below 10 µg/l. In France, the LOQ is 5 µg/l for chromium and chromium compounds. In Germany, the LOQ for total-Cr is 0.5 µg/l based on EN ISO 17294–1. Analytical methods to measure total-Cr include ICP-OES with an approximate LOQ of 2 µg/l (EN ISO 11885) and ICP-MS with a lower limit of application of approximately 1 µg/l (EN ISO 17294–1).

2.4.3.4 Chromium VI (Cr VI)

Chromium VI is not expected at the outlet of the WWTPs.

Overview of WWTP performance on Cr VI
Data on Cr VI were only gathered during the first survey, but not during the second. Out of the 52 directly discharging WWTPs participating in the first survey, 6 reported Cr VI values in the effluent. Of these values, one is of spot-type while the others are given as range-type values (i.e. < X or < LOD). Cr VI concentrations in the influent were only reported in one questionnaire as < LOD. Therefore, no analysis on abatement efficiencies was performed.

Techniques reported to reduce Cr VI emissions
Reduction of Cr VI to Cr III, followed by abatement of total-Cr, was reported in the questionnaires.

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), Cr VI is considered not quantifiable below 10 µg/l. Analytical methods to measure Cr VI include spectrometry with 1,5-diphenylcarbazide in a concentration range of 50–3 000 µg/l (ISO 11083) and flow analysis (FIA/CFA) in a concentration range of 2–2 000 µg/l (EN ISO 23913).

2.4.3.5 Copper (Cu)

The corrosion of pipes and equipment is an important source of copper in waste waters. At some sites, the manufacture of copper-based catalysts, the manufacture of organic copper compounds (e.g. dyes), or the use of catalysts (e.g. ethylene dichloride production via oxychlorination [104, COM 2003]) are a source of copper in waste waters.

Overview of WWTP performance on Cu
Out of a total of 95 directly discharging WWTPs, Cu concentration values in the effluent were reported for 60 WWTPs (or 63 %), and for 20 (or 33 %) of the latter, Cu values in the influent were also reported. Some 14 effluent values were given as below a certain concentration or below the limit of detection (Figure 2.21).

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; LOD = limit of detection; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
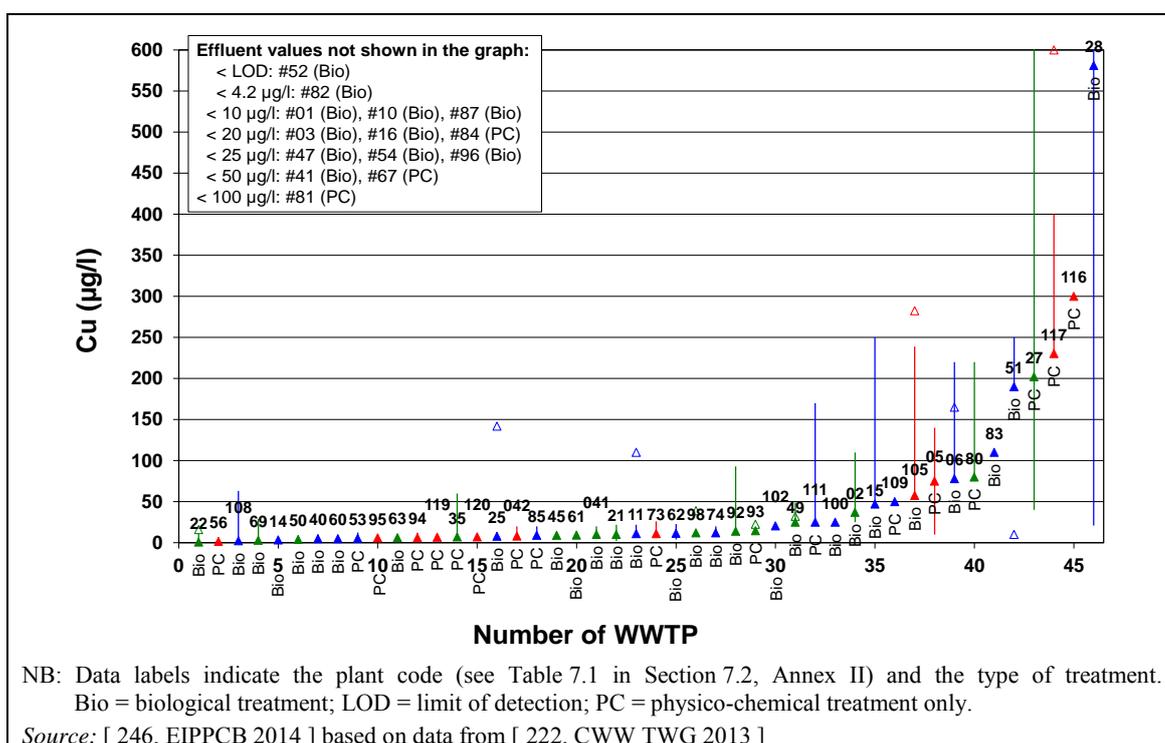
Figure 2.21: Average Cu concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs

Average Cu levels in the effluents are generally ≤ 50 µg/l. Effluent concentrations > 50 µg/l were reported for the WWTPs #05, #06, #27, #28, #51, #80, #83, #105, #116, and #117. Installation #05 produces copper-containing catalysts, installation #06 produces copper-organic dyes, and installations #27 and #80 produce ethylene dichloride. The WWTPs #27, #28, #83, #116, and #117 also showed high emission levels of other metals, while the effluents of the WWTPs #28, #51, #80, and #83 also showed high emission levels of TSS (i.e. > 35 mg/l).

In many cases, biological treatment can be used effectively to abate copper emissions; this is shown by WWTPs #02, #11, and #22 (abatement efficiency > 90 %). However, in the case of WWTP #06, the abatement efficiency is around 50 % due to the presence of copper-organic compounds.

Techniques reported to reduce Cu emissions
The following pretreatment and treatment operations (carried out at the installation(s) from which the waste waters originate or the final WWTP) were reported in the questionnaires:

- precipitation and filtration (with other metals),
- ion exchange (with other metals),
- activated sludge systems.

Fluctuations of emissions around the average (in concentration)
Maximum Cu values reported for 33 WWTPs vary around the average by a factor of 1.0–26, but more generally by a factor of 1.1–8.2 (10th to 90th percentile). The ratio between maximum concentrations and average concentrations tends to be higher for installations with lower average concentrations.

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), Cu is considered not quantifiable below 25 µg/l. In France, the LOQ is 5 µg/l for copper and copper compounds. In Germany, the LOQ for Cu is 0.1 µg/l based on EN ISO 17294–1. Analytical methods to measure Cu include ICP-OES with an approximate LOQ of 2 µg/l (EN ISO 11885) and ICP-MS with a lower limit of application of approximately 1 µg/l (EN ISO 17294–1).

2.4.3.6 Mercury (Hg)

The production of chlorine using the mercury cell technique as well as contaminated sites can be important sources of mercury for final WWTPs. Mercury can adsorb relatively easily onto sludge which has to be controlled if the sludge is incinerated.

Mercury is included in the list of priority hazardous substances in Annex X to the Water Framework Directive [28, Directive 2000/60/EC 2000]. Substances of this annex are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Overview of WWTP performance on Hg
Out of a total of 95 directly discharging WWTPs, Hg concentration values in the effluent were reported for 49 WWTPs (or 52 %), and for 13 (or 27 %) of the latter, Hg values in the influent were also reported. Some 17 effluent values were given as below a certain concentration or below the limit of detection (Figure 2.22).
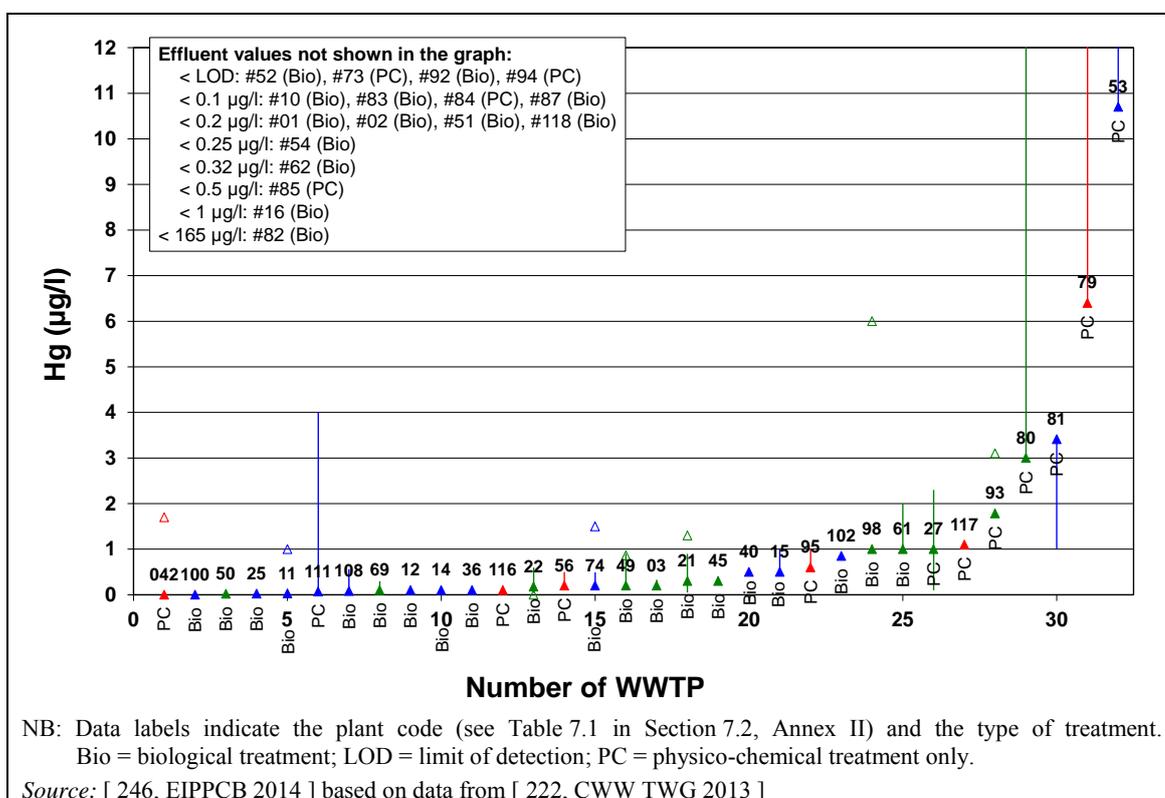
**Figure 2.22: Average Hg concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs**

Average Hg levels in the effluents are generally ≤ 1 µg/l. Effluent concentrations > 1 µg/l were reported for the WWTPs #53, #79, #80, #81, #93, and #117. The mercury cell technique is used at installation #80. The WWTPs #81 and #117 also showed high emission levels of other metals, while WWTP #80 also showed high emission levels of TSS (i.e. > 35 mg/l).

Techniques reported to reduce Hg emissions
The following pretreatment and treatment operations (carried out at the installation(s) from which the waste waters originate or the final WWTP) were reported in the questionnaires:

• precipitation and filtration,
• ion exchange,
• reduction with hydrazine,
• activated carbon,
• activated sludge systems combined with sludge incineration/waste gas treatment.

Fluctuations of emissions around the average (in concentration)
Maximum Hg values reported for 18 WWTPs vary around the average by a factor of 1.0–57, but more generally by a factor of 1.4–6.6 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), Hg is considered not quantifiable below 0.25 µg/l. In France, the LOQ is 0.5 µg/l for mercury and mercury compounds. In Germany, the LOQ for Hg is 0.01 µg/l based on EN ISO 17852 and 0.1 µg/l based on EN 1483. Analytical methods to measure Hg include atomic fluorescence spectrometry in a concentration range of 0.01–10 µg/l (EN ISO 17852) and cold vapour atomic absorption spectrometry in a concentration range of 0.1–10 µg/l (EN 1483).

2.4.3.7 Nickel (Ni)

The corrosion of pipes and equipment is an important source of nickel together with the use of nickel-based catalysts. Process gas scrubber/input from heavy fuel oil or catalyst manufacture is also a source of nickel emissions at some sites. Nickel in soluble form is more difficult to remove.

Nickel is included in the list of priority substances in Annex X to the Water Framework Directive [28, Directive 2000/60/EC 2000]. Substances of this annex are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Overview of WWTP performance on Ni
Out of a total of 95 directly discharging WWTPs, Ni concentration values in the effluent were reported for 49 WWTPs (or 52 %), and for 13 (or 27 %) of the latter, Ni values in the influent were also reported. Nine effluent values were given as below a certain concentration or below the limit of detection (Figure 2.23).

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; LOD = limit of detection; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
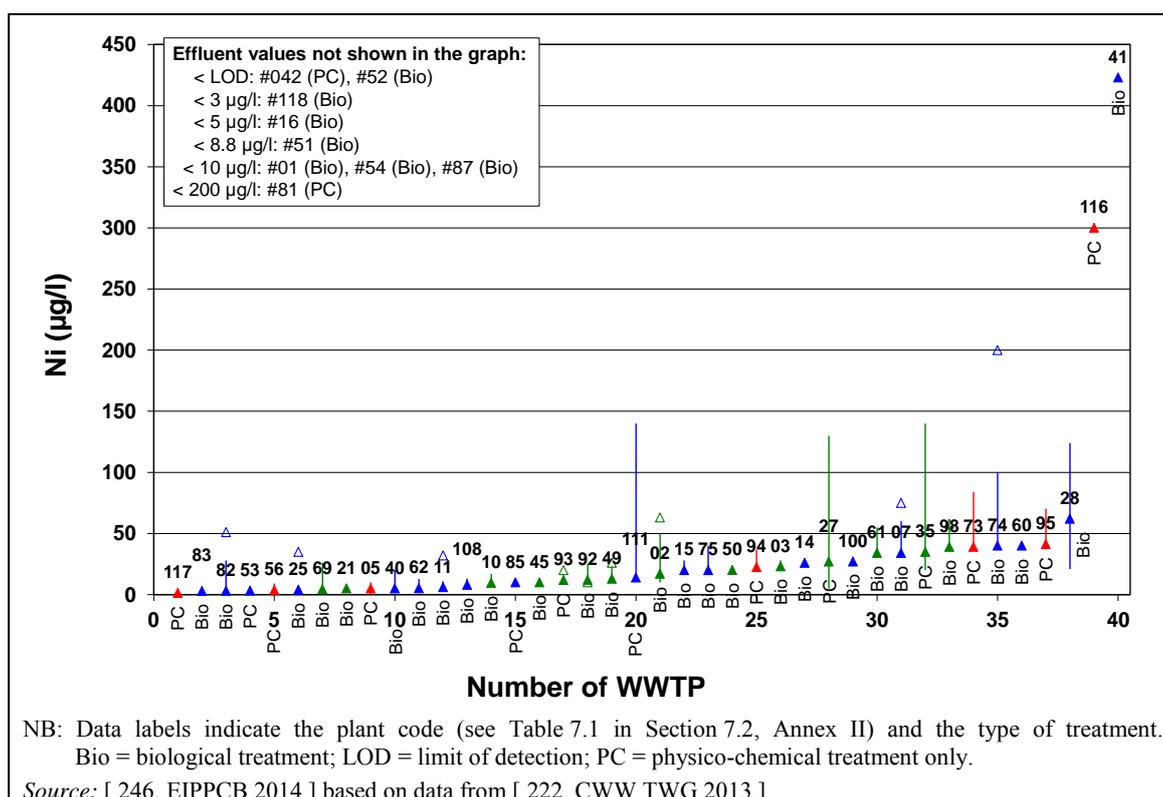
Figure 2.23: Average Ni concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs

Average Ni levels in the effluents are generally ≤ 50 µg/l. Effluent concentrations > 50 µg/l were reported for the WWTPs #28, #41, and #116. The WWTPs #28 and #116 also showed high emission levels of other metals, while the effluent of WWTP #28 also showed high emission levels of TSS (i.e. > 35 mg/l).

Nickel is to some extent abated by biological treatment, albeit less than copper or chromium. This is shown by WWTPs #02, #07, and #11 (abatement efficiency approximately 50–80 %).

Techniques reported to reduce Ni emissions

The following pretreatment and treatment operations (carried out at the installation(s) from which the waste waters originate or the final WWTP) were reported in the questionnaires:

- precipitation and filtration (with other metals),
- ion exchange (with other metals),
- filtration (Raney-Ni),
- activated sludge systems.

Fluctuations of emissions around the average (in concentration)

Maximum Ni values reported for 28 WWTPs vary around the average by a factor of 1.0–10, but more generally by a factor of 1.3–5.1 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)

In Flanders (Belgium) as well as in France, Ni is considered not quantifiable below 10 µg/l. In Germany, the LOQ for Ni is 1 µg/l based on EN ISO 17294–1. Analytical methods to measure Ni include ICP-OES with an approximate LOQ of 2 µg/l (EN ISO 11885) and ICP-MS with a lower limit of application of approximately 1 µg/l (EN ISO 17294–1).

2.4.3.8 Lead (Pb)

Lead is included in the list of priority substances in Annex X to the Water Framework Directive [28, Directive 2000/60/EC 2000]. Substances of this annex are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Overview of WWTP performance on Pb

Out of a total of 95 directly discharging WWTPs, Pb concentration values in the effluent were reported for 43 WWTPs (or 45 %), and for 9 (or 21 %) of the latter, Pb values in the influent were also reported. Some 19 effluent values were given as below a certain concentration or below the limit of detection (Figure 2.24).

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
     Bio = biological treatment; LOD = limit of detection; PC = physico-chemical treatment only.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
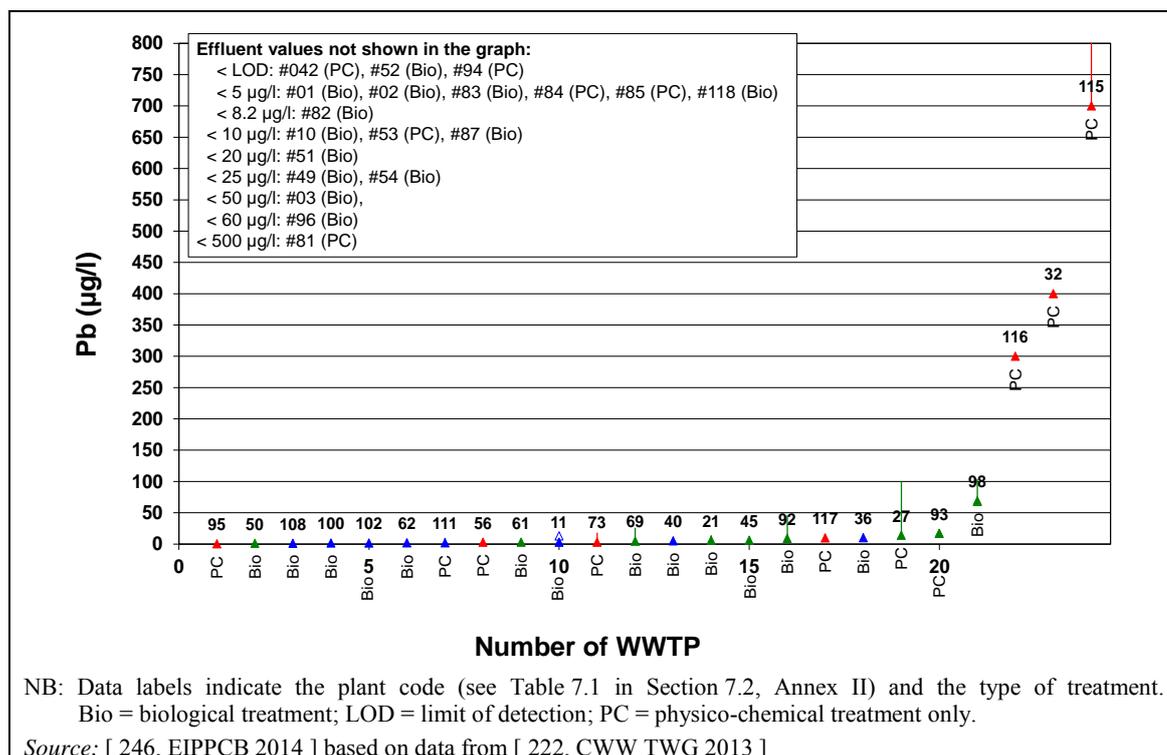
Figure 2.24: **Average Pb concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs**

Average Pb levels in the effluents are generally ≤ 10 µg/l. Effluent concentrations > 10 µg/l were reported for the WWTPs #27, #32, #93, #98, #115, and #116. Installation #32 produces Pb-based PVC stabilisers and installation #115 blends Ca-, Pb-, and Zn-organic stabilisers. The WWTPs #27 and #116 also showed high emission levels of other metals.

Techniques reported to reduce Pb emissions
The following pretreatment and treatment operations (carried out at the installation(s) from which the waste waters originate or the final WWTP) were reported in the questionnaires:

- precipitation with sodium carbonate,
- activated sludge systems.

Fluctuations of emissions around the average (in concentration)
Maximum Pb values reported for 15 WWTPs vary around the average by a factor of 1.0–7.1, but more generally by a factor of 1.2–5.9 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), Pb is considered not quantifiable below 25 µg/l. In France, the LOQ is 5 µg/l for lead and lead compounds. In Germany, the LOQ for Pb is 0.1 µg/l based on EN ISO 17294–1. Analytical methods to measure Pb include ICP-OES with an approximate LOQ of 5 µg/l (EN ISO 11885) and ICP-MS with a lower limit of application of approximately 0.1 µg/l (EN ISO 17294–1).

2.4.3.9   Zinc (Zn)

The corrosion of pipes and equipment (tank insulation, building roofs) is an important source of zinc. Raw materials are also a source of zinc that can ultimately be released into water. Zinc emissions may also originate from the production of viscose [106, COM 2007] or from its use as a corrosion inhibitor in cooling systems [114, COM 2001].

Overview of WWTP performance on Zn
Out of a total of 95 directly discharging WWTPs, Zn concentration values in the effluent were reported for 57 WWTPs (or 60 %), and for 19 (or 33 %) of the latter, Zn values in the influent were also reported. Four effluent values were given as below a certain concentration (Figure 2.25).
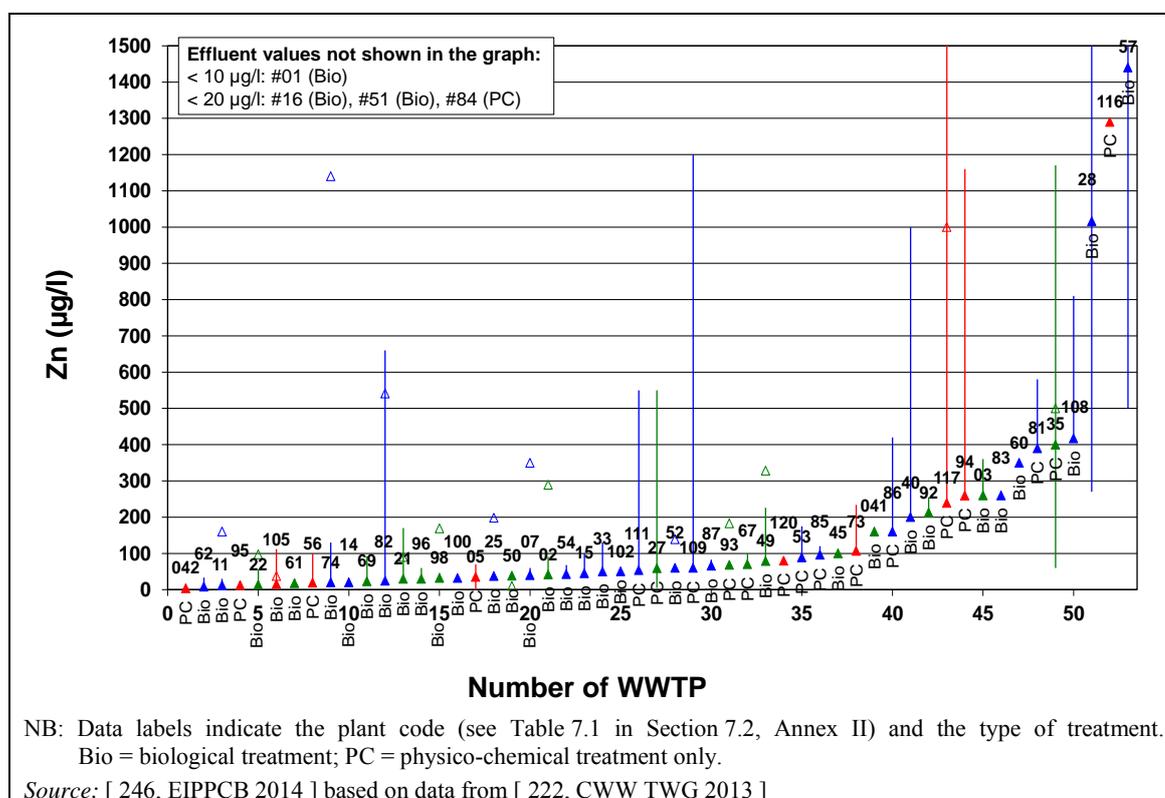
Figure 2.25: Average Zn concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs

Average Zn levels in the effluents are generally ≤ 300 µg/l. Effluent concentrations > 300 µg/l were reported for the WWTPs #28, #35, #57, #60, #81, #108, and #116. At installation #35, the majority of the Zn emissions originate from contaminated groundwater. The WWTPs #28, #81, and #116 also showed high emission levels of other metals.

Zinc is to some extent abated by biological treatment, albeit less than copper or chromium. This is shown by WWTPs #02, #07, #11, #21, #22, and #49 (abatement efficiency approximately 50–90 %).

Techniques reported to reduce Zn emissions
The following pretreatment and treatment operations (carried out at the installation(s) from which the waste waters originate or the final WWTP) were reported in the questionnaires:

- precipitation and filtration (with other metals),
- ion exchange (with other metals),
- activated sludge systems.

Fluctuations of emissions around the average (in concentration)
Maximum Zn values reported for 39 WWTPs vary around the average by a factor of 1.2–27, but more generally by a factor of 1.4–8.6 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), Zn is considered not quantifiable below 25 µg/l. In France, the LOQ is 10 µg/l for zinc and zinc compounds. In Germany, the LOQ for Zn is 1 µg/l based on EN ISO 11885. Analytical methods to measure Zn include ICP-OES with an approximate LOQ of 1 µg/l (EN ISO 11885) and ICP-MS with a lower limit of application of approximately 1 µg/l (EN ISO 17294–1). The operator of WWTP #57 indicated a limit of quantification for zinc of 50 µg/l.

2.4.4　Nitrogen compounds

2.4.4.1　General

While nitrogen is essential to living organisms, excessive concentrations of certain nitrogen compounds in water can lead to significant environmental problems (eutrophication). However, nitrogen, like phosphorus and carbon, is needed in the biological processes of waste water treatment so that organisms that decompose the organic load can reproduce. When the industrial waste waters do not contain enough nitrogen for optimum growth of the organisms, the addition of inorganic nitrogen is carried out. A concentration ratio of $BOD_5/N/P$ of 100/5/1 is often considered optimal for aerobic waste water treatment. For anaerobic treatments steps, the ratio is $BOD_5/N/P = 100/0.5/0.1$ [1, Metcalf and Eddy 1991].

Nitrogen compounds and in particular nitrates are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Nitrogen-containing compounds may originate from the production of organic chemicals (e.g. pharmaceuticals, polymers), inorganic chemicals (e.g. fertilisers), or from the raw materials used in the process (e.g. groundwater contaminated with nitrate).

The measurement of nitrogen-related parameters (i.e. total nitrogen, total inorganic nitrogen, ammonia/ammonium, nitrate and nitrite) is very sensitive to sampling and analytical methods (which is not so much the case for COD or TOC).

The removal of nitrogen is subject to greater variability during operation. The nitrification mechanism as autotrophic is based on very sensitive and slowly growing bacteria compared to the heterotrophic COD/TOC degradation. Therefore, the variability of maximum to average will be much higher compared to COD or TOC performance for example.

Depending on the influent, inorganic nitrogen compounds result partly from the biological treatment process. Therefore, for NH_4-N, NO_2-N, and NO_3-N the concentration in the effluent is generally a more pertinent parameter than the abatement efficiency.

2.4.4.2　Total nitrogen (TN) and total inorganic nitrogen (N_{inorg})

The parameter total nitrogen (TN) includes free ammonia and ammonium (NH_4-N), nitrites (NO_2-N), nitrates (NO_3-N) and organic nitrogen compounds. Dissolved elementary nitrogen (N_2) is not included. TN is frequently measured by combustion with subsequent analysis of nitrogen oxides via chemiluminescence (i.e. total nitrogen bound = TN_b, e.g. according to EN 12260), or by oxidation with peroxodisulphate with subsequent wet-chemical analysis of nitrate (Koroleff method, e.g. according to EN ISO 11905–1). TN can also be determined by summing up the individual concentrations of total Kjeldahl nitrogen (TKN), NO_2-N and NO_3-N.

The parameter total inorganic nitrogen (N_{inorg}) includes free ammonia and ammonium (NH_4-N), nitrites (NO_2-N), and nitrates (NO_3-N). N_{inorg} is usually determined by summing up the individual concentrations of NH_4-N (e.g. measured according to EN ISO 11732), NO_2-N (e.g. measured according to EN ISO 10304–1, EN ISO 13395, or EN 26777), and NO_3-N (e.g. measured according to EN ISO 10304–1 or EN ISO 13395). The measurement of nitrite is more difficult than that of ammonium or nitrate because of its instability and the low concentrations that are typically encountered in effluents.

The parameter total Kjeldahl nitrogen (TKN) includes free ammonia and ammonium (NH_4-N) and organic nitrogen compounds. TKN is measured by sample digestion with sulphuric acid and subsequent stripping of ammonia. The latter is absorbed in a solution of boric acid and titrated (e.g. according to EN 25663). Organically bound nitrogen in the form of azide, azine, azo,

hydrazone, nitrite, nitro, nitroso, oxime, semicarbazone or heterocycles is not determined quantitatively [99, CEN 1993].

From the aforementioned definitions it is apparent that the parameters TN, N_{inorg}, and TKN are not equivalent; therefore, analytical results are non-comparable. By definition, the following applies: $TN \geq N_{inorg}$ and $TN \geq TKN$. For those WWTPs where both TN and N_{inorg} data for the effluent were reported (23 out of a total of 95 directly discharging WWTPs), TN/N_{inorg} ratios range from 0.65 to 2.68 (median 1.3). Values lower than one are theoretically impossible and caused by measurement uncertainties. The ratio becomes higher as the share of organically bound nitrogen increases. In the case of WWTP #70, it was reported that the high ratio of 2.68 is caused by the presence of refractory organic compounds originating from fermentation processes.

A study conducted for the German Federal Environment Agency (UBA DE) on different industrial sectors showed that for the chemical industry, the TN/N_{inorg} ratio was mostly in the range of 1.0–1.4 (median 1.2; 763 samples of 38 effluents) [97, Braun et al. 1999].

In the EU, some Member States use the parameter TN for setting permit conditions while others use the parameter N_{inorg}. Both parameters show advantages and disadvantages. N_{inorg} is generally more difficult to determine as three individual parameters have to be measured (i.e. NH_4-N, NO_2-N, and NO_3-N). Contrary to this, TN can be determined in a single measurement and in combination with the TOC. Compared to N_{inorg}, TN also covers organically bound nitrogen which may contribute to eutrophication. However, the eutrophication potential of organically bound nitrogen is generally considered to be lower than that of inorganic nitrogen species, and some organic nitrogen compounds are poorly biodegradable (e.g. EDTA). Therefore, TN potentially overestimates the bioavailable nitrogen, while N_{inorg} potentially underestimates it [150, Seitzinger and Sanders 1997]. In relation to the techniques used for nitrogen removal, N_{inorg} is considered a better parameter to assess the performance of nitrification/denitrification, while TN additionally reflects the performance of ammonification and any pretreatment of poorly biodegradable organic nitrogen compounds.

Overview of WWTP performance on TN

Out of a total of 63 directly discharging WWTPs with biological treatment, TN concentration values in the effluent were reported for 39 WWTPs (or 62 %), and for 21 (or 54 %) of the latter, TN values in the influent were also reported. One effluent value was given as below a certain concentration (Figure 2.26 and Figure 2.27). Often 24-hour composite samples were taken on a daily basis.
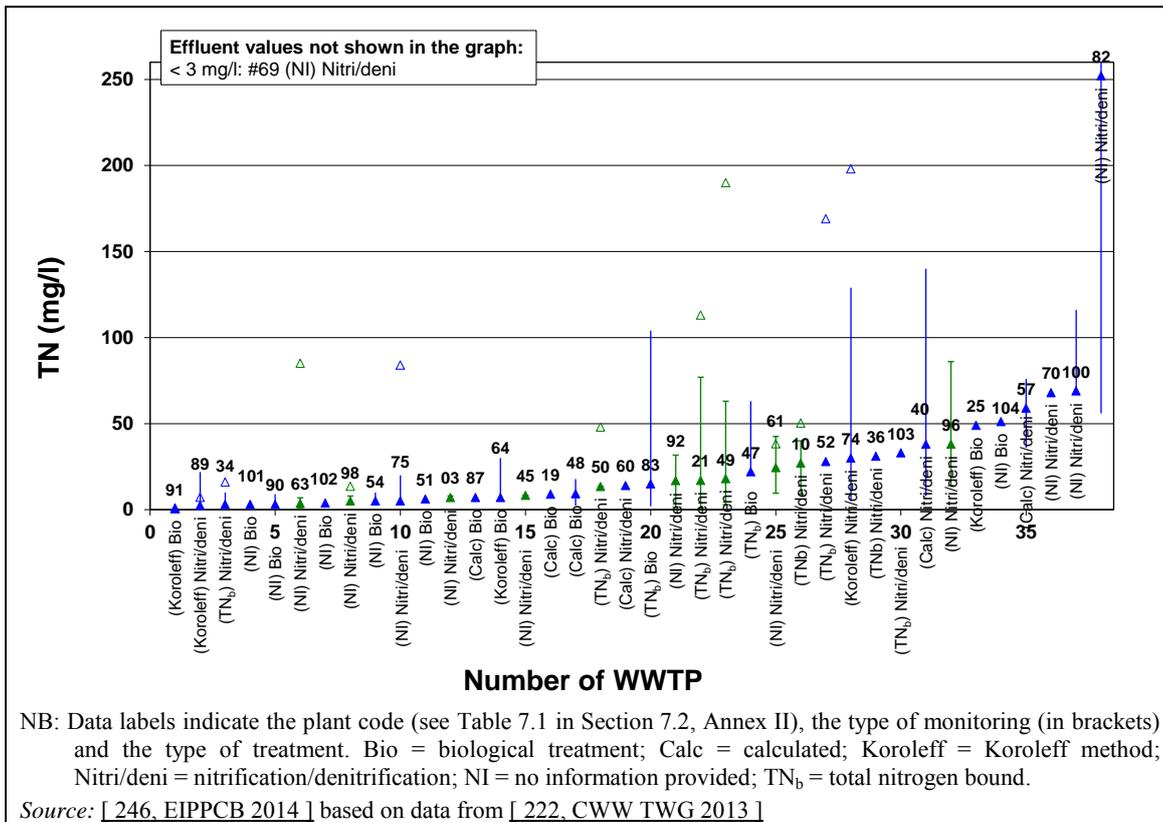
Figure 2.26: Average TN concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs with biological treatment (all biological WWTPs are shown)
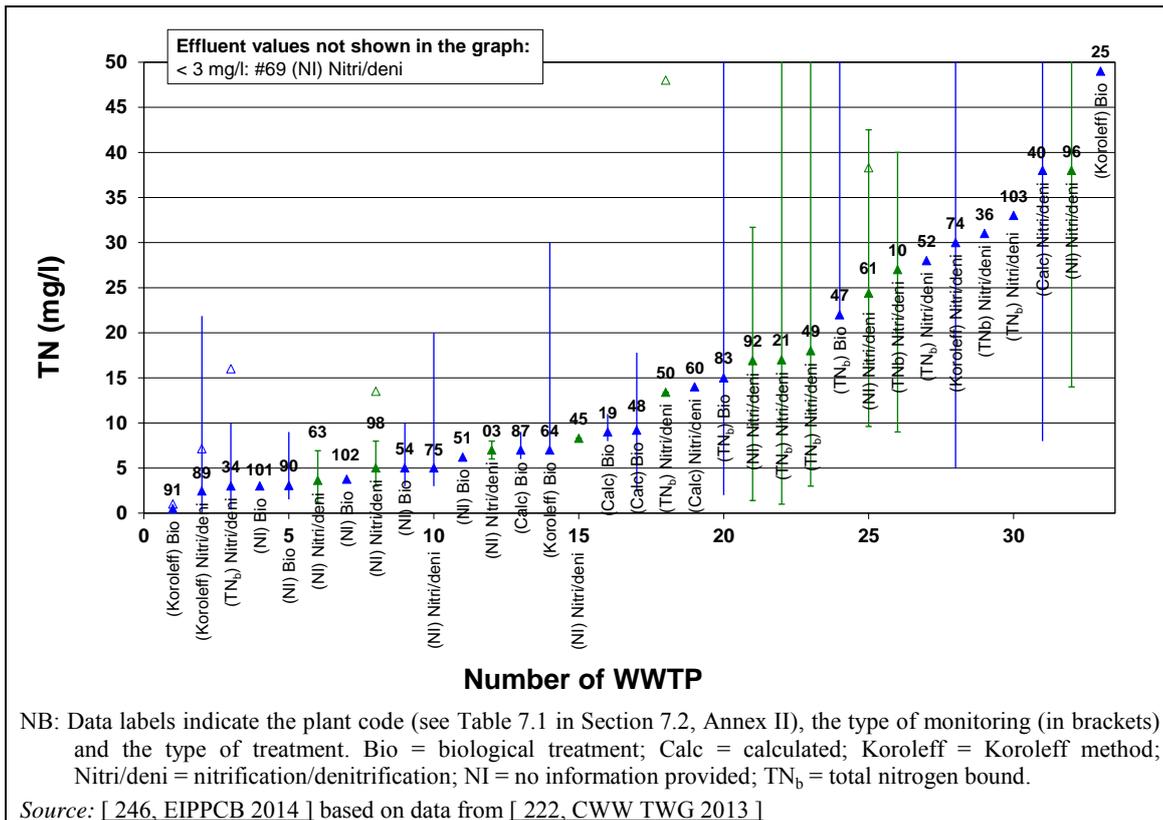
Figure 2.27: Average TN concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs with biological treatment (only biological WWTPs with effluent values ≤ 50 mg/l are shown)

Biological WWTPs showing relatively high BOD_5 and/or TSS values in the effluent (e.g. #25, #57, #70, #82, #100) tend to have higher TN emissions.

Abatement efficiencies for loads reported for 18 biological WWTPs range from 27.8 % to 95.7 %, but more generally from 43.8 % to 91.9 % (10th to 90th percentile) with a median of 78.4 %. Efficiencies reported for loads and concentrations match in the vast majority of cases. Several installations achieve abatement efficiencies higher than 70 % with average effluent concentrations below 40 mg/l.

Overview of WWTP performance on N_{inorg}

Out of a total of 63 directly discharging WWTPs with biological treatment, N_{inorg} concentration values in the effluent were reported for 36 WWTPs (or 57 %), and for 19 (or 53 %) of the latter, N_{inorg} values in the influent were also reported (Figure 2.28 and Figure 2.29). Often 24-hour composite samples were taken on a daily basis.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
    Bio = biological treatment; Nitri/deni = nitrification/denitrification.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
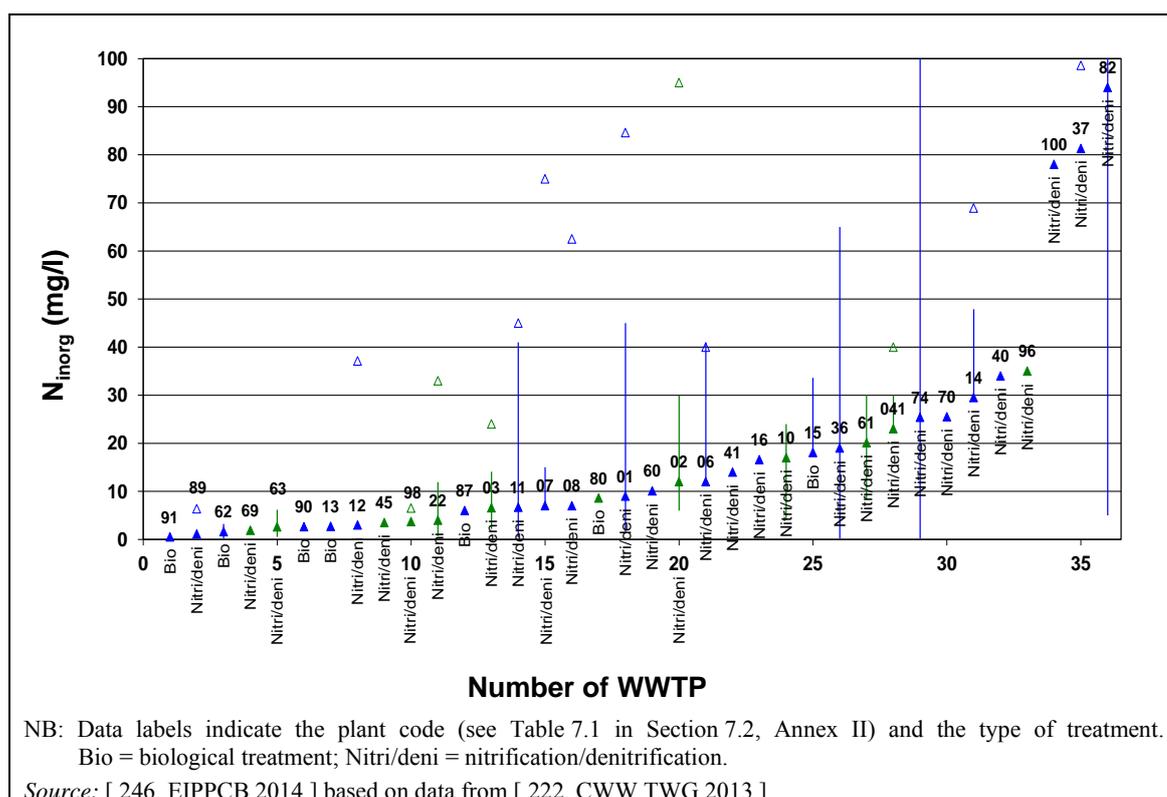
Figure 2.28: Average N_{inorg} concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs with biological treatment (all biological WWTPs are shown)

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
 Bio = biological treatment; Nitri/deni = nitrification/denitrification.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
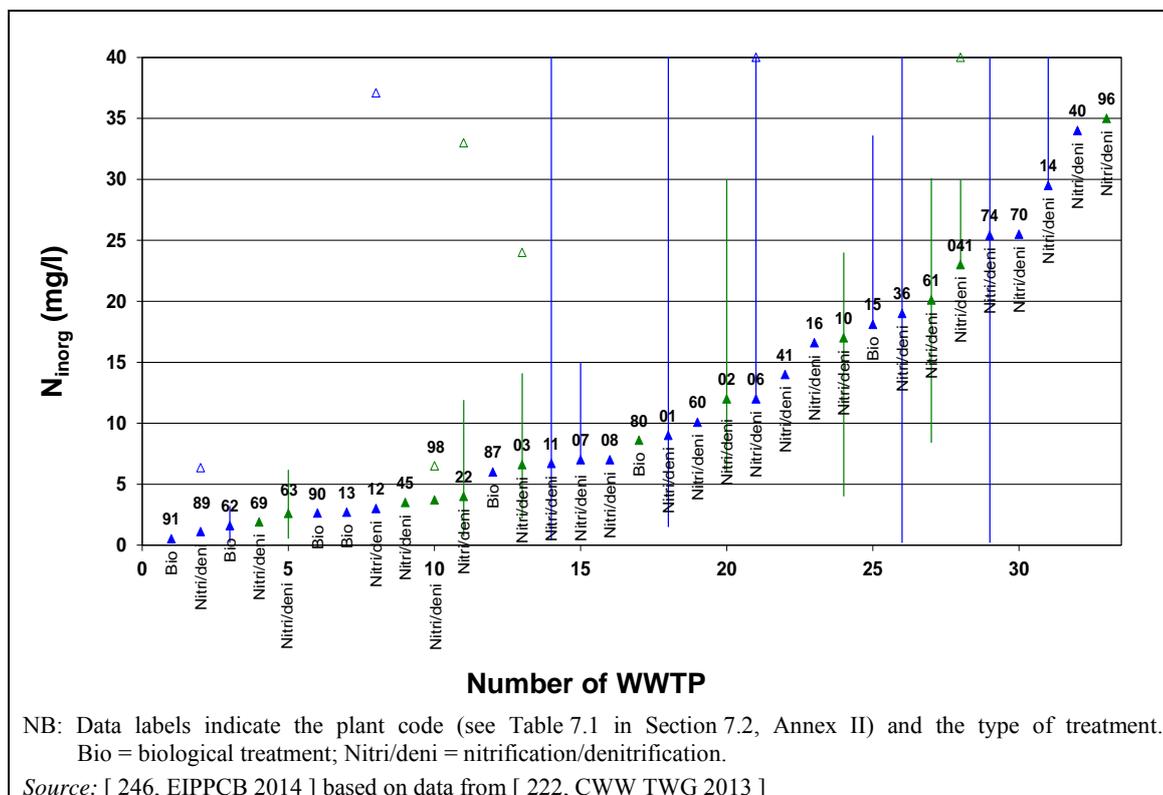
**Figure 2.29: Average N_{inorg} concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs with biological treatment (only biological WWTPs with effluent values ≤ 40 mg/l are shown)**

Biological WWTPs showing either relatively high BOD_5 and/or TSS values in the effluent (e.g. #37, #82, #100) tend to have higher N_{inorg} emissions.

Abatement efficiencies for loads reported for 16 biological WWTPs range from 25.7 % to 93.7 %, but more generally from 46.4 % to 91.3 % (10th to 90th percentile) with a median of 84.4 %. These values are very similar to those reported for TN. Efficiencies reported for loads and concentrations match in the vast majority of cases. Several installations achieve abatement efficiencies higher than 70 % with average effluent concentrations below 35 mg/l.

Techniques reported to reduce nitrogen emissions
A combination of several of the following techniques can be carried out.

- Pretreatment at the installation(s) from which the waste waters originate, e.g.:

    ◦ oxidation with UV radiation (e.g. #02: conversion of EDTA),
    ◦ conversion of cyanide (see Section 2.4.9),
    ◦ stripping (e.g. #02, #15, #50, #61: ammonia),
    ◦ steam distillation (e.g. #50: aniline, nitrobenzene),
    ◦ recycling of nitric acid (e.g. #11, #15),
    ◦ sedimentation (e.g. #63; #69).

Other techniques which are used to treat COD/TOC loads equally apply to organic nitrogen, e.g. wet oxidation with hydrogen peroxide, wet air oxidation, and adsorption.

- Treatments at the final WWTP:

    ◦ nitrification/denitrification,
    ◦ reverse osmosis, evaporation, crystallisation (i.e. #05: recovery of nitrate).

The abatement of nitrate is particularly difficult if, due to the lack of organic compounds in the waste water, no biological WWTP is operated. This situation may arise at inorganic sites (e.g. production of fertilisers: #119 and #120; production of inorganic catalysts: #05).

Fluctuations of emissions around the average (in concentration)
Maximum TN values reported for 29 WWTPs vary around the average by a factor of 1.2–8.9, but more generally by a factor of 1.3–4.3 (10th to 90th percentile). Maximum N_{inorg} values reported for 26 WWTPs vary around the average by a factor of 1.3–6.1, but more generally by a factor of 1.4–4.9 (10th to 90th percentile). TN and N_{inorg} fluctuations are slightly higher than COD and TOC fluctuations.

Limits of detection (LOD) and quantification (LOQ)
TN: In Flanders (Belgium), TN is considered not quantifiable below 2 mg/l. In Spain, the LOQ for TN is 10 mg/l. In Germany, the LOQ for TN is 1 mg/l based on EN 12260. EN 12260 specifies a method for quantifying TN by combustion and detection of nitrogen oxides using chemiluminescence (TN_b). Typical limits of detection are around 0.5 mg/l. EN ISO 11905–1 specifies a method using oxidative digestion with peroxodisulphate to nitrate which is then quantified. A typical limit of detection is 0.02 mg/l. The method can be used in the case of COD < 120 mg/l and TOC < 40 mg/l. Otherwise samples are diluted. ISO 29441 specifies a method for the determination of total nitrogen after in-line UV digestion and flow analysis with spectrometric detection. Mass concentrations range from 2 mg/l to 20 mg/l, but other concentration ranges are possible, e.g. 0.2 mg/l to 2 mg/l.

N_{inorg}: In Flanders (Belgium), N_{inorg} is considered not quantifiable below 2 mg/l. In Germany, the LOQ for N_{inorg} was reported to be about 1 mg/l.

NH_4-N: see Section 2.4.4.3.

NO_2-N: In Flanders (Belgium), nitrite is considered not quantifiable below 0.1 mg/l (corresponding to 0.03 mg/l of NO_2-N). EN ISO 10304–1 (ion chromatography) gives a lower limit of application of 0.05 mg/l (corresponding to 0.02 mg/l of NO_2-N).

NO_3-N: In Flanders (Belgium), nitrate is considered not quantifiable below 0.5 mg/l (corresponding to 0.1 mg/l of NO_3-N). EN ISO 10304–1 (ion chromatography) gives a lower limit of application of 0.1 mg/l (corresponding to 0.02 mg/l of NO_3-N).

TKN: In Spain, the LOQ for TKN is 10 mg/l. EN 25663 is based on selenium-catalysed mineralisation with concentrated sulphuric acid with a limit of detection of 1 mg/l.

Parameters that affect performance
Ammonification
The first step in the removal of nitrogen during biological treatment is conversion of organic nitrogen to ammonia/ammonium. For domestic sewage, where organic nitrogen consists of urea and faecal material, this already takes place to a certain extent while travelling through sewer pipes. In the case of waste waters from chemical installations, some organic N might be recalcitrant to ammonification (e.g. EDTA).

The ratio of ammonia (NH_3) versus ammonium (NH_4^+) depends on pH and temperature. At conditions typical for most biological waste water treatment plants (pH of 6 to 8.5, temperatures of 10 to 40 ºC), far more ammonium than ammonia is present.

Nitrification
Nitrification is a two-step process. Bacteria known as *Nitrosomonas* convert ammonia and ammonium to nitrite. Next, bacteria called *Nitrobacter* finish the conversion of nitrite to nitrate. The reactions are generally coupled and proceed rapidly from the nitrite to the nitrate form; therefore, nitrite levels at any given time are usually low (i.e. < 1 mg/l).

These bacteria known as 'nitrifiers' are strict 'aerobes', meaning they must have free dissolved oxygen to perform their work. Nitrification occurs only under aerobic conditions at dissolved oxygen levels of 1.0 mg/l or more. At dissolved oxygen concentrations of less than 0.5 mg/l, the growth rate is minimal. Nitrification requires a long retention time, a low food to microorganism ratio (F/M), a high mean cell residence time (measured as mean cell residence time or sludge age), and adequate buffering (alkalinity).

The nitrification process produces acid. This acid formation lowers the pH of the biological population in the aeration tank and can cause a reduction of the growth rate of nitrifying bacteria. The optimum pH for *Nitrosomonas* and *Nitrobacter* is between 7.5 and 8.5; most treatment plants are able to effectively nitrify with a pH of 6.5 to 7.0. Nitrification stops at a pH below 6.0. The nitrification reaction (that is, the conversion of ammonium to nitrate) consumes 7.1 mg/l of alkalinity as $CaCO_3$ for each mg/l of NH_4-N oxidised. An alkalinity of no less than 50–100 mg/l is required to ensure adequate buffering.

Water temperature also affects the rate of nitrification. Nitrification reaches a maximum rate at temperatures between 30 °C and 35 ºC. At temperatures of 40 ºC and higher, nitrification rates fall to nearly zero. At temperatures below 20 ºC, nitrification proceeds at a slower rate, but will continue at temperatures of 10 ºC or lower. However, if nitrification is lost, it will not resume until the temperature increases to well over 10 ºC. Some of the most toxic compounds to nitrifiers include cyanide, thiourea, phenol and metals such as silver, mercury, nickel, chromium, copper and zinc. Nitrifying bacteria can also be inhibited by nitrous acid and free ammonia.

Denitrification

The biological reduction of nitrate (NO_3^-) to nitrogen gas (N_2) by facultative heterotrophic bacteria is called denitrification. 'Heterotrophic' bacteria need a carbon source as food to live. 'Facultative' bacteria can get their oxygen by taking dissolved oxygen out of the water or by taking it from nitrate molecules.

Denitrification occurs when oxygen levels are depleted and nitrate becomes the primary oxygen source for microorganisms. The process is performed under anoxic conditions, when the dissolved oxygen concentration is less than 0.5 mg/l, ideally less than 0.2 mg/l. When bacteria break apart nitrate to gain the oxygen, the nitrate is reduced to nitrous oxide (N_2O), and, in turn, nitrogen gas (N_2). Since nitrogen gas has low water solubility, it escapes into the atmosphere as gas bubbles. Free nitrogen is the major component of air, thus its release does not cause any environmental concern.

Optimum pH values for denitrification are between 7.0 and 8.5. Denitrification is an alkalinity-producing process. Approximately 3.0 to 3.6 mg/l of alkalinity (as $CaCO_3$) is produced per mg/l of nitrate, thus partially mitigating the lowering of pH caused by nitrification in the mixed liquor.

Since denitrifying bacteria are facultative organisms, they can use either dissolved oxygen or nitrate as an oxygen source for metabolism and oxidation of organic matter. If dissolved oxygen and nitrate are present, bacteria will use the dissolved oxygen first. That is, the bacteria will not lower the nitrate concentration. Denitrification occurs only under anaerobic or anoxic conditions.

Another important aspect of denitrification is the requirement for carbon; that is, the presence of sufficient organic matter to drive the denitrification reaction. Organic matter may be in the form of raw waste water, or supplemental carbon. Conditions that affect the efficiency of denitrification include nitrate concentration, anoxic conditions, presence of organic matter, pH, temperature, alkalinity and the effects of trace metals. Denitrifying organisms are generally less sensitive to toxic chemicals than nitrifiers, and recover from toxic shock loads quicker than nitrifiers.

Temperature affects the growth rate of denitrifying organisms, with a greater growth rate at higher temperatures. Denitrification can occur between 5 °C and 40 ºC, and these rates increase with temperature and type of organic source present. The highest growth rate can be found when using methanol or acetic acid. A slightly lower rate using raw waste water will occur, and the lowest growth rates are found when relying on endogenous carbon sources at low water temperatures. Three installations report the addition of external carbon sources to ensure/improve the denitrification process (i.e. #63: methanol, #45 and #69: acetic acid).

Nitrification/denitrification is further described in Section 3.3.2.3.5.5.

<u>Relationship between performance and techniques used as reported in the questionnaires</u>
The performance of nitrification/denitrification depends on a number of plant operating conditions as described above. Most of these operating conditions were not asked for in the questionnaires. Therefore, it is difficult to establish relationships with the reported performance levels.

2.4.4.3 Ammonium (as NH$_4$-N)

Ammonium can be present in the influent of final WWTPs. Ammonia/ammonium can also be formed as a first step in the removal of nitrogen in biological WWTPs (i.e. ammonification, see Section 2.4.4.2). Ammonium is on the one hand assimilated into bacterial cells (leading thus to net growth) and on the other hand oxidised to nitrite and nitrate (nitrification). Nitrifying organisms are present in almost all aerobic biological treatment processes, but usually their numbers are limited.

Free ammonia in concentrations above about 0.2 mg/l can cause fatalities in several species of fish [89, Sawyer et al. 2003].

<u>Overview of WWTP performance on NH$_4$-N</u>
Out of a total of 95 directly discharging WWTPs, NH$_4$-N concentration values in the effluent were reported for 56 WWTPs (or 59 %), and for 33 (or 59 %) of the latter, NH$_4$-N values in the influent were also reported (Figure 2.30 and Figure 2.31). Often 24-hour composite samples were taken on a daily basis.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; Nitri/deni = nitrification/denitrification; PC = physico-chemical treatment only.
*Source:* [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
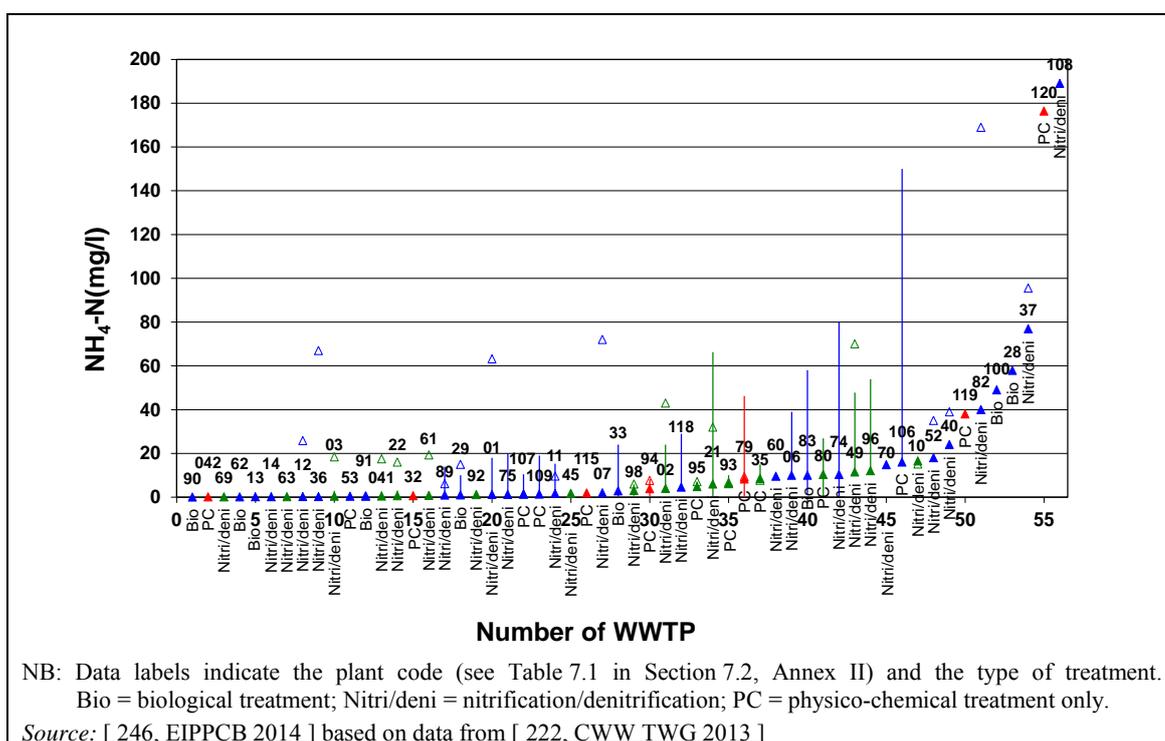
Figure 2.30: Average NH$_4$-N concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (all WWTPs are shown)

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
Bio = biological treatment; Nitri/deni = nitrification/denitrification; PC = physico-chemical treatment only.

Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
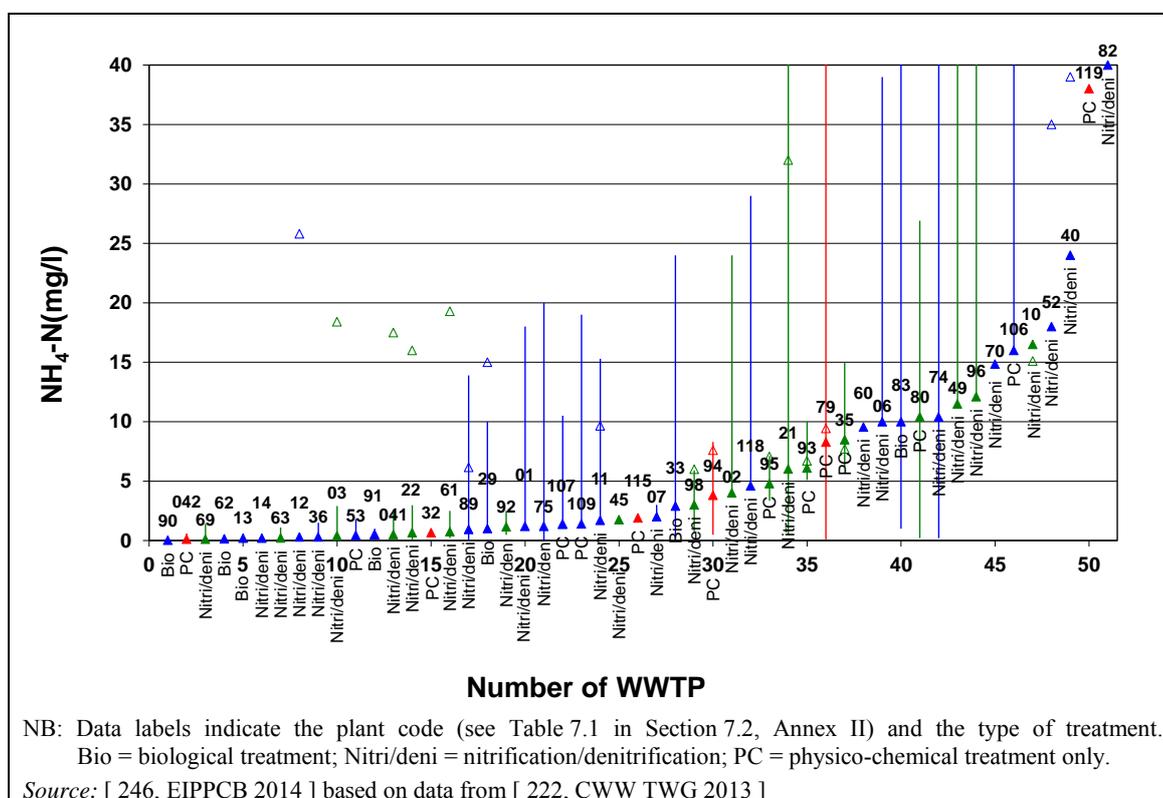
Figure 2.31: Average NH$_4$-N concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (only WWTPs with effluent values ≤ 40 mg/l are shown)

Biological WWTPs showing either relatively high BOD$_5$ and/or TSS values in the effluent (e.g. #28, #37, #82, #100, #108) tend to have higher NH$_4$-N emissions.

Abatement efficiencies for loads reported for 23 WWTPs range from -9.3 % to 99.6 %, but more generally from 13.8 % to 98.1 % (10th to 90th percentile) with a median of 90.5 %. Efficiencies reported for loads and concentrations match in the vast majority of cases. At WWTP #10 (abatement efficiency -9.3 %), the NH$_4$-N concentration in the effluent is higher than in the influent due to ammonification and inhibition of nitrification because of high chloride levels. At the installations #119 and #120, nitrogen-containing fertilisers are produced. Due to the absence of organic compounds in the waste water, the final WWTP only applies physico-chemical treatment.

Techniques reported to reduce ammonium emissions
A combination of the following techniques can be used:

- pretreatment at the installation(s) from which the waste waters originate, e.g. stripping (e.g. #21, #61);
- treatments at the final WWTP: nitrification/denitrification.

Fluctuations of emissions around the average (in concentration)
Maximum NH$_4$-N values reported for 48 WWTPs vary around the average by a factor of 1.0–16.7, but more generally by a factor of 1.6–11.5 (10th to 90th percentile). NH$_4$-N fluctuations are significantly higher than COD and TOC fluctuations. This is due to the higher sensitivity of nitrifying bacteria to changes of temperature, seasonal effects, change of production, start-ups and shutdowns.

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), NH_4-N is considered not quantifiable below 0.20 mg/l. In Germany, the LOQ for NH_4-N is 0.05 mg/l based on EN ISO 11732. This standard is based on flow analysis and gives an approximate lower limit of application of 0.1 mg/l. Literature reports that NH_4-N can be determined over a range of 0.02–2 mg/l by an automated phenate procedure.

Parameters that affect performance
Suspended-growth nitrification and denitrification processes are very much dependent on temperature, pH, dissolved oxygen, residence time and sludge age.

The dynamic of ammonium removal by bacteria is different to the removal of COD due to the differing nature of the bacteria involved. It is therefore important to know when changes in production can occur so as to possibly take the necessary measures to minimise ammonium emissions, if the interactions are known and the measures applicable.

Relationship between performance and techniques used as reported in the questionnaires
The sensitivity of nitrification causes large variations in emissions as can be seen in Figure 2.30 and Figure 2.31.

2.4.5   Total phosphorus (TP)

Organophosphorus compounds as well as phosphates are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Phosphorus is present in waste waters in inorganic and organic forms. The inorganic forms are orthophosphates (i.e. HPO_4^{2-}/$H_2PO_4^-$) and polyphosphates. Organically bound phosphorus is usually of minor importance. Polyphosphates can be used as a means of controlling corrosion. Phosphorus discharge has to be controlled in the same way as nitrogen discharge in order to avoid eutrophication of surface waters. It was reported that, to avoid algal blooms under summer conditions, the critical level of inorganic phosphorus is near 0.005 mg/l.

Microorganisms utilise phosphorus for cell synthesis and energy transport. As a result, 10–30 % of the influent phosphorus is removed during traditional biological treatment [1, Metcalf and Eddy 1991]. Biological phosphorus removal can be enhanced by the presence of an anaerobic tank (nitrate and oxygen are absent) prior to the aeration tank. Under these conditions a group of heterotrophic bacteria, called polyphosphate-accumulating organisms are selectively enriched in the bacterial community within the activated sludge. These bacteria accumulate large quantities of polyphosphate within their cells and the removal of phosphorus is said to be enhanced. Therefore, these bacteria not only consume phosphorus for cellular components but also accumulate large quantities of polyphosphate within their cells; up to a fraction of 5–7 % of the biomass. Enhanced biological phosphorus removal is used in a number of urban WWTPs, but very rarely in WWTPs on chemical sites.

When the industrial waste waters do not contain enough phosphorus for optimum growth of the organisms used in treatment, the addition of inorganic phosphates is carried out (e.g. #13, #16, #22, #29, #40, #41, #50, #51, #61, #75, #82, #83, #87, #89, #91, and #100; see also Section 2.4.4.1). Apart from the biological waste water treatment, sludge digestion may also require the addition of nutrients.

Overview of WWTP performance on TP
Out of a total of 95 directly discharging WWTPs, TP concentration values in the effluent were reported for 60 WWTPs (or 63 %), and for 31 (or 52 %) of the latter, TP values in the influent were also reported (Figure 2.32 and Figure 2.33). Often 24-hour composite samples were taken on a daily basis.
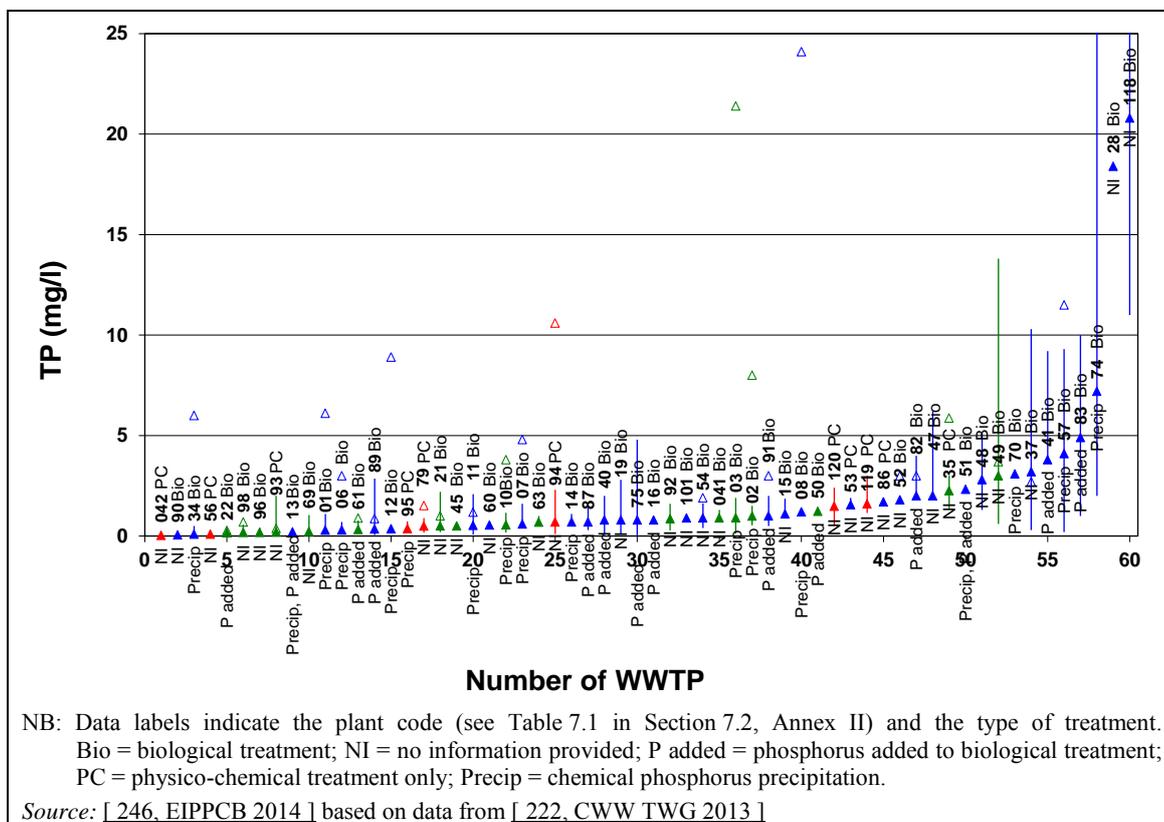
Figure 2.32: Average TP concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (all WWTPs are shown)
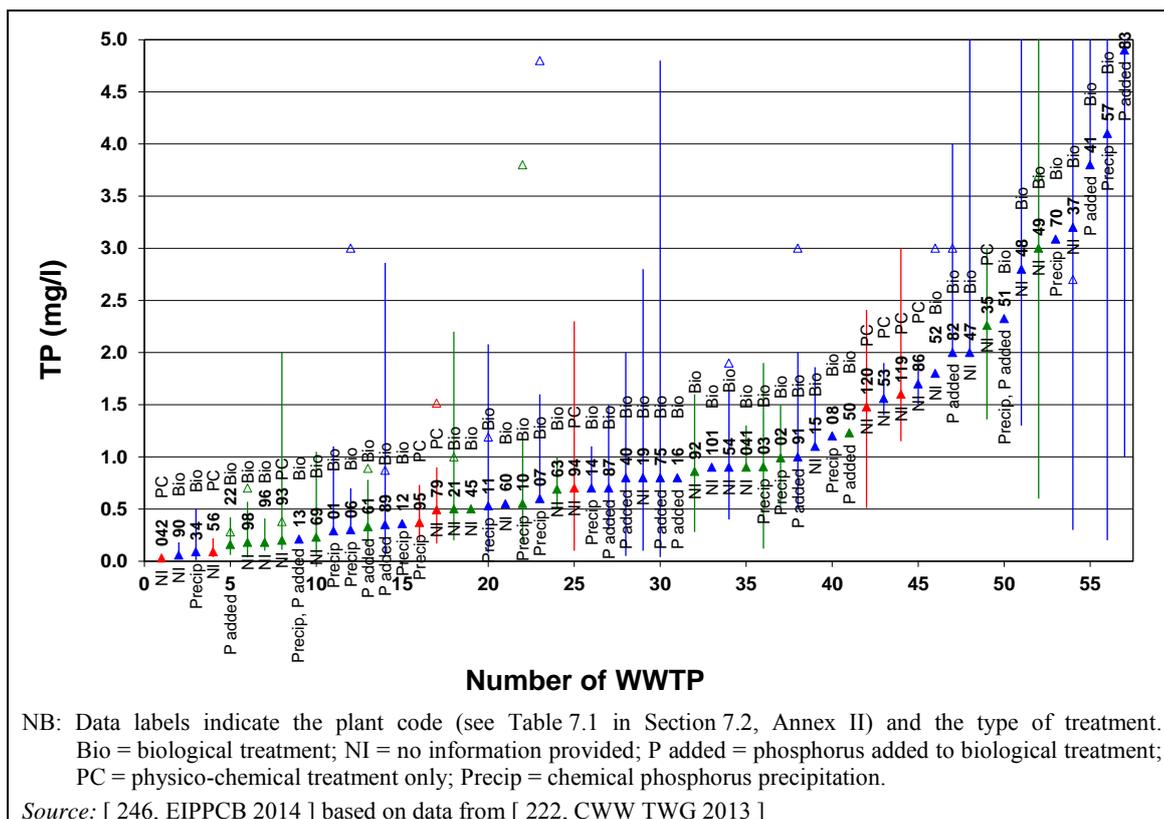
Figure 2.33: Average TP concentrations (mostly yearly averages) in the influents and effluents of directly discharging WWTPs (only WWTPs with effluent values ≤ 5 mg/l are shown)

Average TP levels in the effluents are generally ≤ 3 mg/l. Effluent concentrations > 3 mg/l were reported for the WWTPs #28, #37, #41, #48, #49, #57, #70, #74, #83, and #118. The WWTPs #28, #37, #48, #57, #70, #74, and #83 also showed high emission levels of TSS (i.e. > 35 mg/l). High TP concentrations in the influents to the final WWTP (i.e. > 50 mg/l) were reported for the WWTPs #14 (production of dyes and pigments), #70 (production of pharmaceuticals, fermentation processes), #74 (production of organophosphorus insecticides), and #95 (production of fertilisers). Many WWTPs using chemical phosphorus precipitation achieve TP values in the effluent of < 1.5 mg/l, including some WWTPs with high TP levels in the influent (i.e. #14 (biological treatment)) and #95 (physico-chemical treatment only)). Similarly, WWTPs that add phosphorus to the biological treatment generally achieve TP values in the effluent of < 1.5 mg/l.

Abatement efficiencies for loads reported for 21 WWTPs range from -13.3 % to 98.8 %, but more generally from 46.0 % to 97.7 % (10th to 90th percentile) with a median of 77.7 %. These values suggest that chemical precipitation of phosphorus is often carried out in addition to biological phosphorus removal. At WWTP #37 (abatement efficiency -13.3 %), the TP concentration in the effluent is higher than in the influent due to the addition of TP as a nutrient to the biological treatment.

Techniques reported to reduce TP emissions
A combination of several of the following techniques is used:

- pretreatment at the installation(s) from which the waste waters originate, e.g. precipitation;
- treatments at the final WWTP by one of the following techniques:

  ◦ biological phosphorus removal (P incorporated into the cell biomass);
  ◦ precipitation in biological WWTPs (e.g. with lime, ferric chloride or alum, e.g. #01, #02, #03, #06, #07, #08, #10, #11, #12, #13, #14, #33, #34, #36, #51, #57, #70, #74, #76), before, during or after the biological treatment;
  ◦ precipitation in physico-chemical WWTPs (e.g. #95).

Chemical precipitation for phosphorus removal increases the volume of sludge produced (on average by 26 %, [86, Sedlak 1991]) and often results in a sludge with poor settling and dewatering characteristics. Also, precipitation with metal salts can depress the pH. If nitrification is required, additional alkalinity will be consumed and the pH will drop further. With biological phosphorus removal, the need for chemical addition is reduced or eliminated. Other benefits of biological phosphorus removal are: reduced sludge production, improved sludge settleability and dewatering characteristics, reduced oxygen requirements, and reduced process alkalinity requirements.

Fluctuations of emissions around the average (in concentration)
Maximum TP values reported for 49 WWTPs vary around the average by a factor of 1.1–74.6, but more generally by a factor of 1.5–4.8 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
Several standards for the determination of TP exist: EN ISO 6878 (2004) specifies methods for the determination of different types of phosphates including TP after digestion. The methods are applicable to all kinds of water. Phosphorus concentrations within the range of 0.005–0.8 mg/l may be determined. A solvent extraction procedure allows smaller phosphorus concentrations to be determined with a limit of detection of about 0.5 µg/l. EN ISO 15681−1 and −2 (2003) specify flow methods (FIA/CFA) for the determination of TP for the mass concentration range from 0.1 mg/l to 10 mg/l. Another possibility is to use ICP-OES with an approximate LOQ of 0.009 mg/l (EN ISO 11885).

Parameters that affect performance
Phosphorus emissions are very sensitive to the C/N/P ratio. In many cases, TP emissions not only reflect emissions from production but also dosing to biotreatment. In some periods, the dosing level has to be raised to ensure a stable bacterial growth.

The precipitation of phosphates is dependent on, for example, type and concentration of flocculants, pH value, mixing regime, and residence time.

At some WWTPs, chemical phosphorus precipitation alternates with phosphorus dosing, depending on the influent composition (e.g. #13, #51).

The key to enhanced biological phosphorus removal is the exposure of the microorganisms to alternating anaerobic and aerobic conditions [1, Metcalf and Eddy 1991]. Care has to be taken that phosphorus released during sludge treatment (e.g. during sludge digestion due to cell hydrolysis) does not re-enter into the waste water treatment.

Relationship between performance and techniques used as reported in the questionnaires
The performance of biological phosphorus removal and the precipitation of phosphates depends on a number of plant operating conditions as described above. Most of these operating conditions were not asked for in the questionnaires. Therefore, it is difficult to establish relationships with the reported performance levels.

2.4.6   Phenols

Persistent hydrocarbons and persistent and bioaccumulable organic substances (some phenols present such characteristics) are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Phenol itself can be quite toxic to bacteria in concentrated solutions. However, literature reports that phenol can serve as food for aerobic bacteria without serious toxic effects at levels as high as 500 mg/l.

A phenol threshold concentration of 200 mg/l was reported to have an inhibitory effect on the activated sludge process [1, Metcalf and Eddy 1991].

Overview of WWTP performance on phenols
Data on the concentration of phenols were only gathered during the first survey, but not during the second. Out of a total of 52 directly discharging WWTPs participating in the first survey, concentration values for phenols in the effluent were reported for 11 WWTPs (or 21 %), and for 3 (or 27 %) of the latter, concentration values for phenols in the influent were also reported. One effluent value was given as below a certain concentration (Figure 2.34). Many averaging periods reported were yearly.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
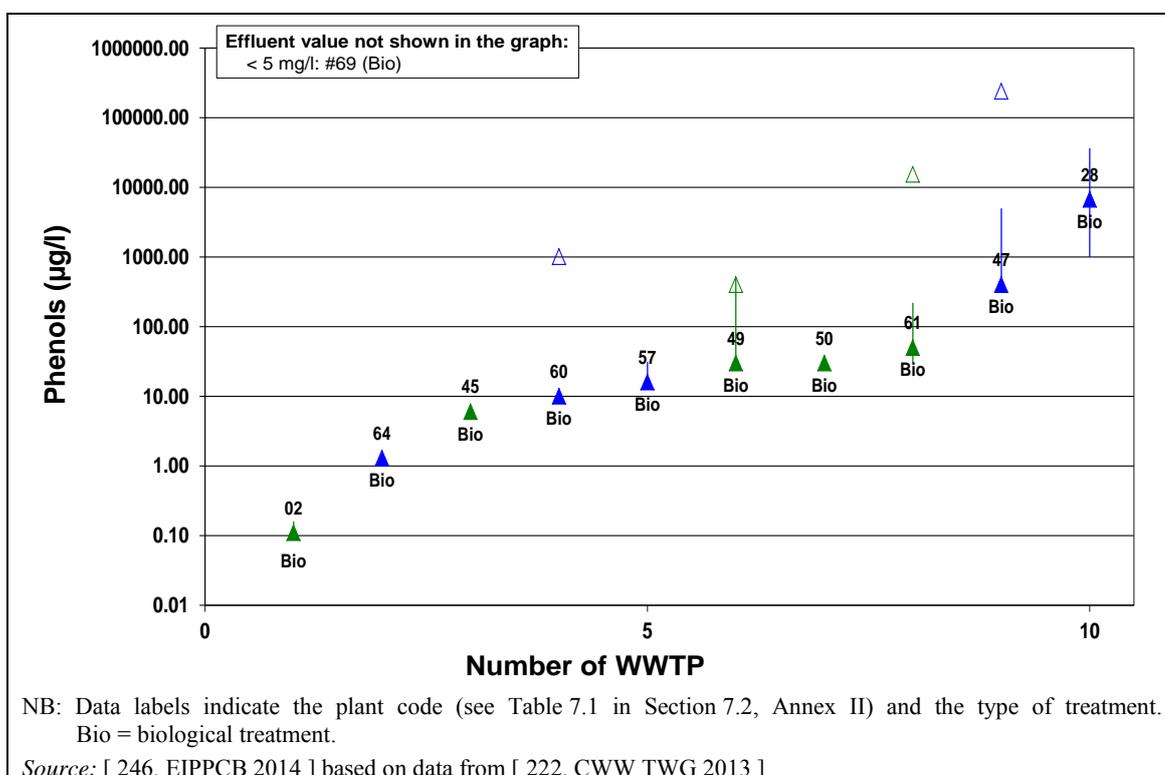
Figure 2.34: Average concentrations of phenols in the influents and effluents of directly discharging WWTPs

The reported concentrations of phenols were determined by various methods and are therefore not comparable.

At two WWTPs, concentrations of phenols in the effluent are above 100 µg/l and even above 1 000 µg/l at one of them (i.e. #28).

High concentrations of phenols in the influent correspond to final WWTPs treating waste waters from installations where phenolic compounds are used/produced (e.g. #47, #61).

Abatement efficiencies reported for five WWTPs are in the range of 90–99.9 %. Four WWTPs reported abatement efficiencies > 99 %.

Techniques reported to reduce emissions of phenols
A combination of several of the following techniques were reported to be used:

- pretreatment at the installation(s) from which the waste waters originate, e.g.:

  ◦ extraction (e.g. #57, #61),
  ◦ adsorption with activated carbon (e.g. #50);

- treatments at the WWTP:

  ◦ biological treatment using the CMAS process (e.g. #28, #47, #50, #57, #60, #61, #64).

Fluctuations of emissions around the average (in concentration)
Maximum values of phenols reported for six WWTPs vary around the average by a factor of 1.5–16.7.

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), phenol is considered not quantifiable below 0.2 µg/l. Several international standards for determining phenols exist. The phenol index can be measured by ISO 6439 (1990) which gives procedures for drinking waters, surface waters, brines (saline waters), domestic waters and industrial waters. After a preliminary distillation, the test samples are analysed according to specific application by the direct colorimetric method (4-aminoantipyrine) and by the chloroform extraction method. Another possibility is to use flow analysis (flow injection analysis – FIA – and continuous flow analysis – CFA) according to EN ISO 14402 (1999). The phenol index is an operationally defined parameter. Therefore the results largely depend on the procedure applied.

Specific phenols can be determined by:

- ISO 81651–1 (1992) and ISO 8165–2 (1999): selected monovalent phenols;
- EN ISO 17495 (2003): nitrophenols;
- EN ISO 18857–1 (2006): alkylphenols;
- ISO 18857–2 (2009): alkylphenols, their ethoxylates and bisphenol A;
- ISO 24293 (2009): isomers of nonylphenol;
- EN 12673 (1998): chlorophenols.

Results from the different analytical methods are difficult to compare. Regarding the phenol index, the recovery of distinct phenols varies considerably. In addition, different national standards for measuring the phenol index are in use, e.g. DIN 38409–16, NF T 90–204, APAT IRSA 5070 A1/A2.

Parameters that affect performance
The removal of phenols in activated sludge processes is reported to be sensitive to temperature; a better performance is achieved in cold rather than warm weather.

Relationship between performance and techniques used as reported in the questionnaires
The conventional treatment methods adopted for the removal of phenols depend require respecting its toxic limits and adequate acclimatisation of the biomass. The trickling filter and the activated sludge process are generally in use for the treatment of phenolic waste water. The removal of phenols is effective only up to a certain level. Some discharged effluent standards are set at 0.1 mg/l. Thus, the conventional methods may not be sufficient to bring down the phenol concentration to such a low level in the treated effluent.

2.4.7 Chloride

Chloride is not included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Chloride occurs in all natural waters in widely varying concentrations (very high in seas and oceans, on average 19 g/l). Freshwater organisms can be harmed by excessive chloride concentrations, e.g. EC_{10} (48 h) and EC_{50} (48 h) values of 3.9 g/l and 12 g/l, respectively, were reported for the standardised fish egg test with *danio rerio*.

The literature reports that chloride concentrations > 1 g/l have a negative effect on the biological removal of phosphorus in WWTPs and that chloride concentrations > 10 g/l have negative effects on the nitrification in WWTPs.

Overview of WWTP performance on chloride
Data on chloride were only gathered during the first survey, but not during the second. Out of a total of 52 directly discharging WWTPs participating in the first survey, chloride concentration values in the effluent were reported for 22 WWTPs (or 42 %), and for 9 (or 41 %) of the latter,

chloride values in the influent were also reported. One effluent value was given as below a certain concentration (Figure 2.35). Many averaging periods reported were yearly.
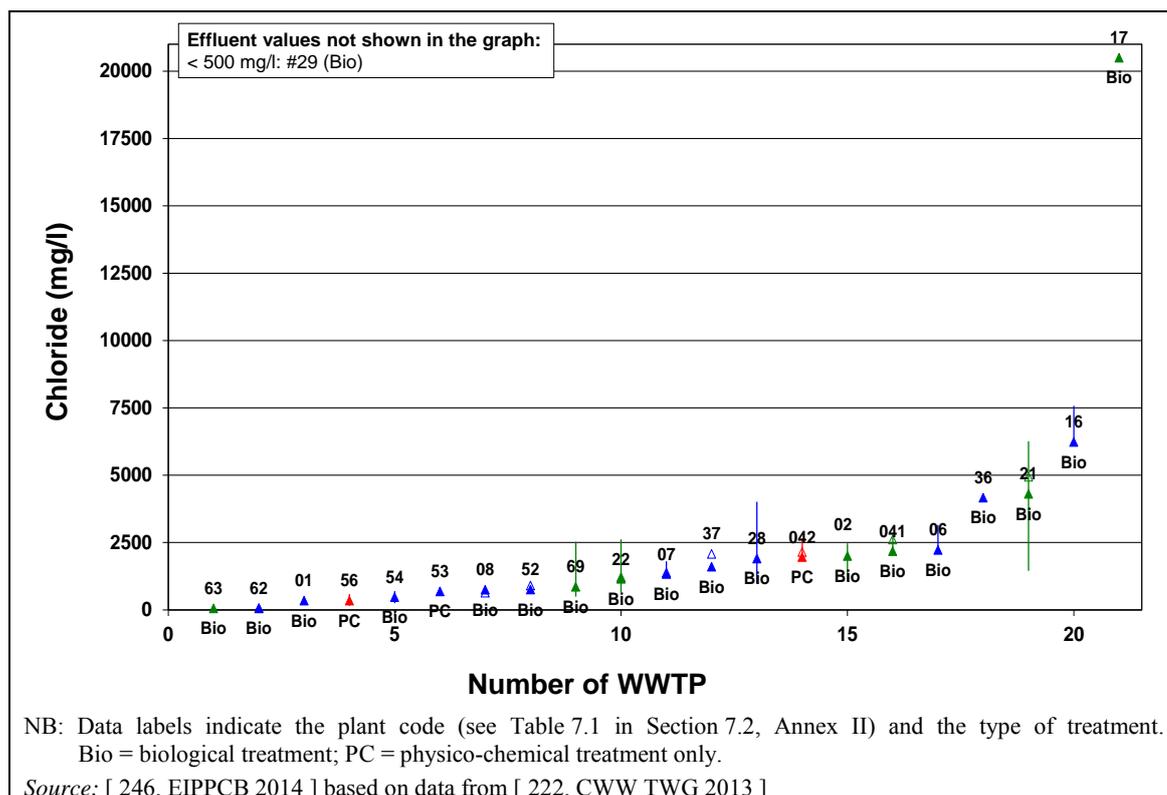
Figure 2.35: Average chloride concentrations in the influents and effluents of directly discharging WWTPs

Average chloride levels in the effluents are generally ≤ 5 g/l. Abatement efficiencies reported are generally low, below 30 %. Therefore, the WWTPs usually have no impact on chloride abatement.

Techniques reported to reduce chloride emissions
Waste waters loaded with chloride can be treated by nanofiltration or reverse osmosis, but this technique is not used by any of the directly discharging WWTPs.

Fluctuations of emissions around the average (in concentration)
Maximum chloride values reported for 15 WWTPs vary around the average by a factor of 1.2–3.0, but more generally by a factor of 1.2–2.2 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), chloride is considered not quantifiable below 25 mg/l. Several international standards for measuring chloride exist. ISO 9297 (1989) uses titration with silver nitrate and chromate indicator (Mohr's method) and is applicable to concentrations between 5 mg/l and 150 mg/l. Due to many interferences, the method is not applicable to heavily polluted waters of low chloride content. EN ISO 10304–1 (2007) uses ion chromatography for the determination of chloride with a lower application limit of 0.1 mg/l.

Parameters that affect performance
Not relevant since the final WWTP is not generally used to reduce chloride.

Relationship between performance and techniques used as reported in the questionnaires
Chloride is basically not removed by biological and most physico-chemical treatments in the WWTPs. On the contrary, chloride is often added to the waste waters, either during neutralisation/acidification using hydrochloric acid or during flocculation using aluminium or iron chloride.

Biological WWTPs (carbon removal) work even at very high salt concentrations (< 5 %). However, high salt concentrations may hinder nitrification. Chloride is usually only considered in regard to the impact on the performance of the WWTP, e.g. sedimentation, velocity of bacterial growth, or the interference on analytics, e.g. AOX measurements and biotests.

2.4.8 Sulphate

Sulphate is not included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

The sulphate ion is one of the major anions occurring in natural waters. It is of importance because of its cathartic effect on humans when it is present in excessive amounts. It is important to control sulphate in the influent of waste water treatment plants because of the potential to create odour (formation of hydrogen sulphide) and corrosion problems in sewers (by oxidation of hydrogen sulphide to sulphuric acid). Freshwater organisms can be harmed by excessive sulphate concentrations.

Overview of WWTP performance on sulphate
Data on sulphate were only gathered during the first survey, but not during the second. Out of a total of 52 directly discharging WWTPs participating in the first survey, sulphate concentration values in the effluent were reported for 18 WWTPs (or 35 %), and for 6 (or 33 %) of the latter, sulphate values in the influent were also reported. One effluent value was given as below a certain concentration (Figure 2.36). Many averaging periods reported were yearly.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
    Bio = biological treatment; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
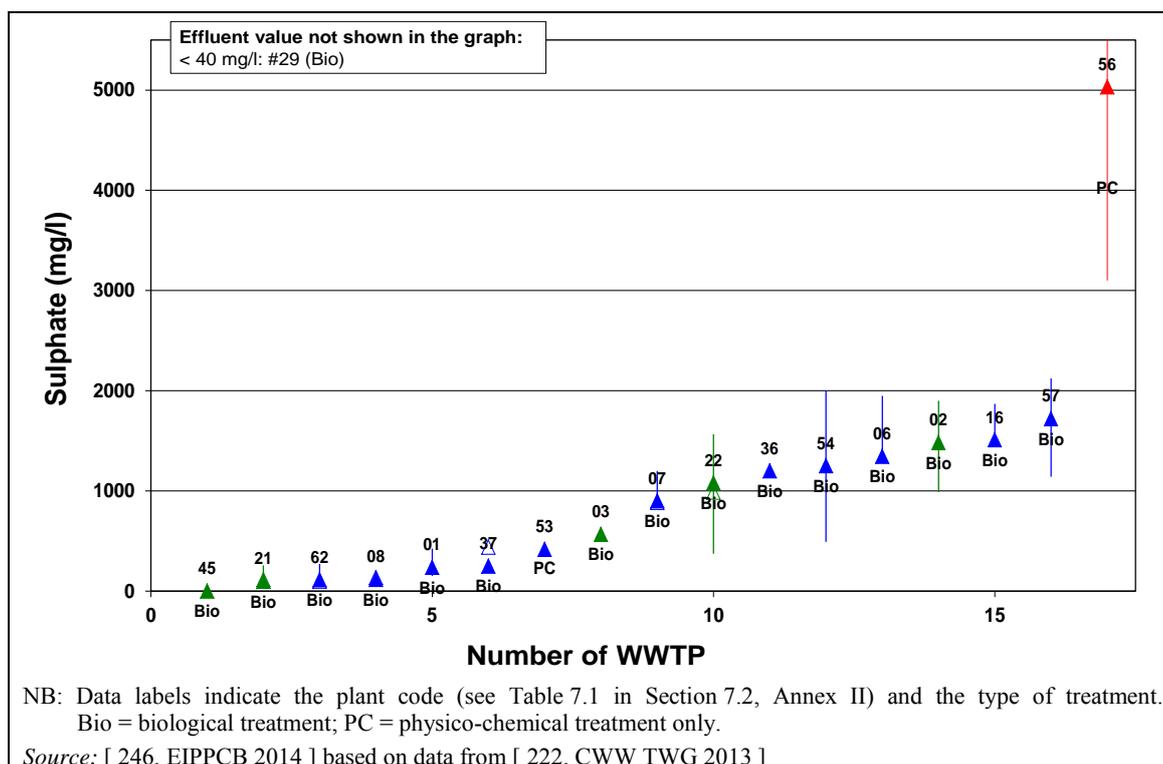
Figure 2.36: Average sulphate concentrations in the influents and effluents of directly discharging WWTPs

Average sulphate levels in the effluents are generally ≤ 2 g/l. Abatement efficiencies reported are generally low and below 43 %. Therefore, the WWTPs usually have no impact on sulphate abatement.

Techniques reported to reduce sulphate emissions
Waste waters loaded with sulphate can be treated by nanofiltration and reverse osmosis, but this technique is not used by any of the directly discharging WWTPs.

Fluctuations of emissions around the average (in concentration)
Maximum sulphate values reported for 12 WWTPs vary around the average by a factor of 1.2–2.6, but more generally by a factor of 1.2–2.3 (10th to 90th percentile).

Limits of detection (LOD) and quantification (LOQ)
In Flanders (Belgium), sulphate is considered not quantifiable below 25 mg/l. Several international standards for measuring sulphate exist. EN ISO 10304–1 (2007) uses ion chromatography for the determination of sulphate with a lower application limit of 0.1 mg/l. ISO 22743 (2006) specifies a continuous flow analysis (CFA) method for the determination of sulphate in various types of water including waste water. The method is applicable to samples with a mass concentration of 30 mg/l to 300 mg/l. Other concentration ranges are applicable, provided they cover exactly one decade of concentration units (e.g. 100 mg/l to 1 000 mg/l).

Parameters that affect performance
Not relevant since the final WWTP is not generally used to reduce sulphate.

Relationship between performance and techniques used as reported in the questionnaires
Sulphate is generally not removed by biological and most physico-chemical treatments in the WWTPs, with the exception of the addition of calcium hydroxide or lime which may lead to the precipitation of calcium sulphate. On the contrary, sulphate is often added to the waste waters either during neutralisation/acidification using sulphuric acid or during flocculation using aluminium or iron sulphate.

2.4.9 Cyanides (free)

Cyanides are included in the indicative list of polluting substances in Annex II to the IED (2010/75/EU) to be taken into account for setting emission limit values [5, Directive 2010/75/EU 2010].

Cyanides can be present in water in dissolved or particulate form. They can be found as cyanide ions (CN^-), hydrogen cyanide (HCN), complex bound cyanides, organically bound cyanides, e.g. nitriles and cyanohydrins, and other inorganic forms, e.g. cyanogen chloride (chlorocyan, NCCl), cyanogen bromide (NCBr) and trimethylsilyl cyanide ($(CH_3)_3SiCN$). Free cyanide is commonly designated as CN^-, although it is actually defined as the total of CN^- and HCN.

Many cyanide-containing compounds are highly toxic, but some are not. For example, organic cyanides and hexacyanoferrates (ferrocyanide and ferricyanide, where the cyanide is already tightly bound to an iron ion) have low toxicities. The most dangerous cyanides are inorganic cyanides such as hydrogen cyanide and salts derived from it, such as potassium cyanide (KCN) and sodium cyanide (NaCN), among others. Also, some compounds readily release HCN or the cyanide ion (CN^-), such as trimethylsilyl cyanide upon contact with water and cyanoacrylates upon pyrolysis. The primary concern regarding aqueous cyanide is that it could volatilise, especially when the pH is below 8.

The cyanide ion (CN^-) has a relatively short half-life because it can serve as a source of energy for aerobic bacteria, provided the concentration is kept below its toxic threshold to the aerobic bacteria. In the US, a drinking water standard sets a limit of 0.2 mg/l to protect against

industries with direct discharges to natural waters. To put this into context, EU drinking water standards set a limit of 0.05 mg/l (for total cyanide).

Overview of WWTP performance on free cyanides
Data on free cyanides were only gathered during the first survey, but not during the second. Of a total of 52 directly discharging WWTPs participating in the first survey, free cyanide concentration values in the effluent were reported for seven WWTPs (or 13 %), and for one (or 14 %) of the latter, free cyanide values in the influent were also reported. One effluent value was given as below a certain concentration (Figure 2.37). Some averaging periods reported were yearly averages.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
  Bio = biological treatment; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
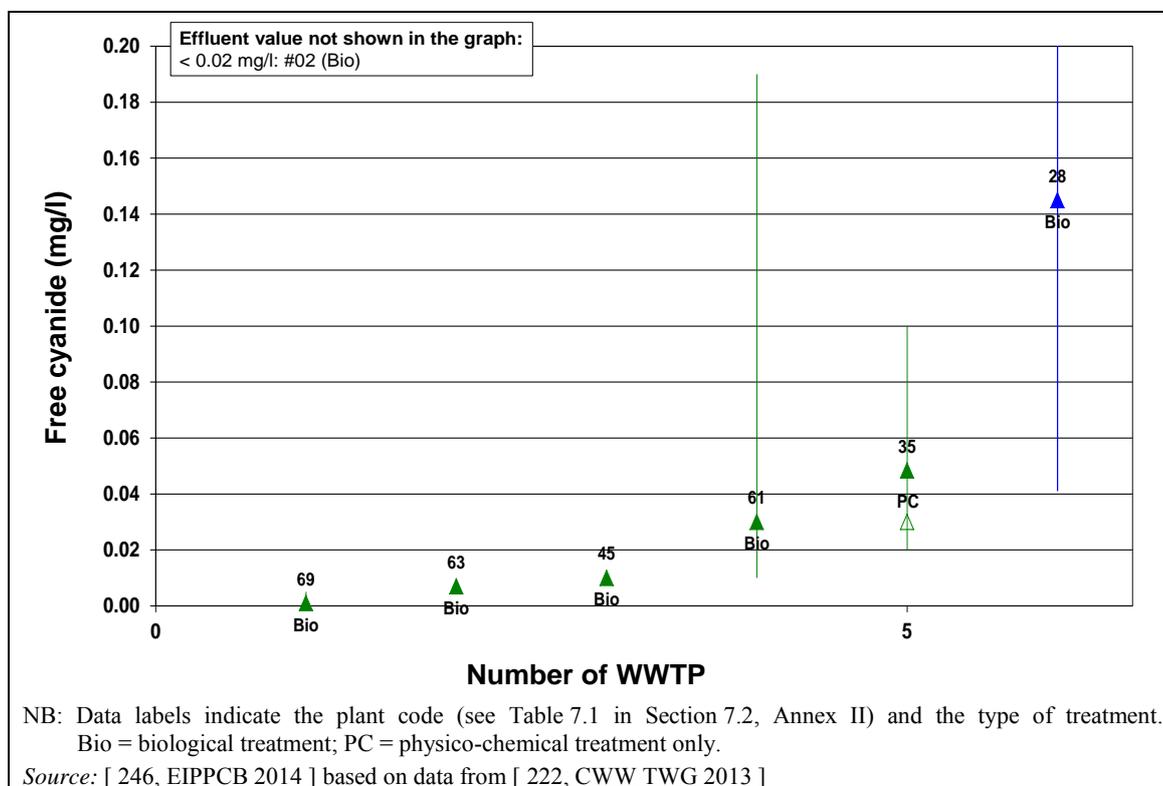
Figure 2.37: Average free cyanide concentrations in the influents and effluents of directly discharging WWTPs

Average levels of free cyanide in the effluents are generally ≤ 0.2 mg/l.

Abatement efficiencies could not be indicated due to the lack of influent data.

Techniques reported to reduce cyanide emissions
At an adequately low level, cyanides are biodegradable in an adapted WWTP (see [105, COM 2006]). The rate of biodegradation depends on the activity and adaptation of the WWTP. When influent concentrations are high (in the range of 4–5 mg/l), there is a risk of toxicity for the bacteria of the biological treatment.

The following pretreatment techniques were reported:

- conversion to glyconitrile with formaldehyde and sodium hydroxide (e.g. #02, #28);
- oxidation with hydrogen peroxide (e.g. #35);
- complexation with iron and oxidation with ozone (e.g. #61);
- oxidation with hypochlorite (e.g. #57, #63);
- oxidation under alkaline conditions (e.g. #69).

Fluctuations of emissions around the average (in concentration)
Maximum values of free cyanide reported for four WWTPs vary around the average by a factor of 2.1–6.3.

Limits of detection (LOD) and quantification (LOQ)
Cyanides are usually measured as a sum parameter. Depending on the analytical method used, more or fewer cyanide species are included. Easily released cyanide is usually understood as the sum of all cyanide compounds which release hydrogen cyanide at a pH value of 4, which includes alkaline and alkaline earth cyanides, as well as the cyanide bound in weak metal cyanide complexes (e.g. $Zn(CN)_4^{2-}$). Total cyanide usually includes all inorganic forms of cyanides including complex bound cyanides and also cyanohydrins. Nitriles, cyanates (OCN^-), thiocyanates (SCN^-), and cyanogen chloride are not included.

In Flanders (Belgium), free cyanides are considered not quantifiable below 0.01 mg/l. Several international standards for measuring cyanides exist: ISO 6703–1 (1984) describes the determination of total cyanide, ISO 6703–2 (1984) the determination of easily released cyanide, and ISO 6703–3 (1984) the determination of cyanogen chloride. ISO 6703–2 consists of three methods with different application ranges: the photometric method with pyridine/barbituric acid: 0.002 mg/l to 0.025 mg/l; the titrimetric method using the Tyndall effect: > 0.005 mg/l; and the titrimetric method using an indicator: > 0.05 mg/l. EN ISO 14403–1 and –2 (2012) describe a method for the determination of total cyanide and free cyanide by flow analysis. The methods are based on digestion with UV radiation in the case of total cyanide and spectrophotometric detection. The methods are applicable to various types of water in the range of 0.002–0.5 mg/l.

Parameters that affect performance
Not relevant since the final WWTP is not generally used to reduce cyanides.

Relationship between performance and techniques used as reported in the questionnaires
As reported in [105, COM 2006], due to their toxicity, cyanides are removed from rich and lean waste water streams, e.g. by pH adjustment and oxidative destruction with H_2O_2. Depending on the individual case, it may also be possible to enable safe degradation of cyanides in a biological WWTP. The use of NaOCl for pretreatment has the potential for the formation of AOX. Reconditioning of different cyanide-loaded streams can enable reuse and the substitution of raw materials. Cyanides occurring in waste water streams together with high COD loads can be pretreated oxidatively by techniques such as wet oxidation with O_2 under alkaline conditions. In such cases, cyanide levels of < 1 mg/l are achievable in the treated waste water stream.

2.4.10   Toxicity

2.4.10.1   General

A relatively small amount of toxicity data was submitted during the first survey. The data submitted mainly concern German installations with limited data corresponding to French (i.e. #41 and #57) and Italian installations (i.e. #69).

Fish/fish egg tests, daphnia tests, algae tests and luminescent bacteria tests are all common test methods for the toxicity assessment of complex waste water streams. They are often used to obtain additional information that can be gained from sum parameter measurements (COD, TOC, BOD, AOX, etc.). With toxicity tests it is possible to assess the possible hazardous character of waste water in an integrated manner and to assess all synergistic effects which may occur because of the presence of a lot of different individual pollutants. Apart from the possibility of using the toxicity tests to estimate potential hazardous effects on the ecosystem/surface water, these tests can help to protect or to optimise biological waste water treatment plants (see [101, COM 2016]).

Several international standards for the measurement of toxicity in waste waters exist, e.g. EN ISO 6341 (1996) for daphnia magna, EN ISO 8692 (2004) for algae, EN ISO 113481–1 to –3 (2008) for luminescent bacteria, EN ISO 20079 (2006) for duckweed, and EN ISO 15088 (2008) for zebrafish eggs (see Section 3.2.2.2).

Toxicity tests require expertise that may not be available in all plants/regions yet and they are not amenable to be carried out very frequently.

Techniques reported to reduce toxicity
There are no specific techniques to reduce toxicity in waste waters. All treatment steps, as summarised in the sections above, which lead to the reduction of the concentration of toxic organic and inorganic compounds (e.g. metals, ammonia, cyanides, phenols, and toxic parts of COD/TOC) are applicable.

2.4.10.2 Fish or fish egg toxicity

Overview of WWTP performance on fish or fish egg toxicity
Data on toxicity were only gathered during the first survey, but not during the second. Out of a total of 52 directly discharging WWTPs participating in the first survey, fish or fish egg toxicity values in the effluent were reported for 18 WWTPs (or 35 %) (Figure 2.38). Averaging periods are generally not indicated. Average values are based on a number of measurements spanning from 5 to 21.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment.
    Bio = biological treatment; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
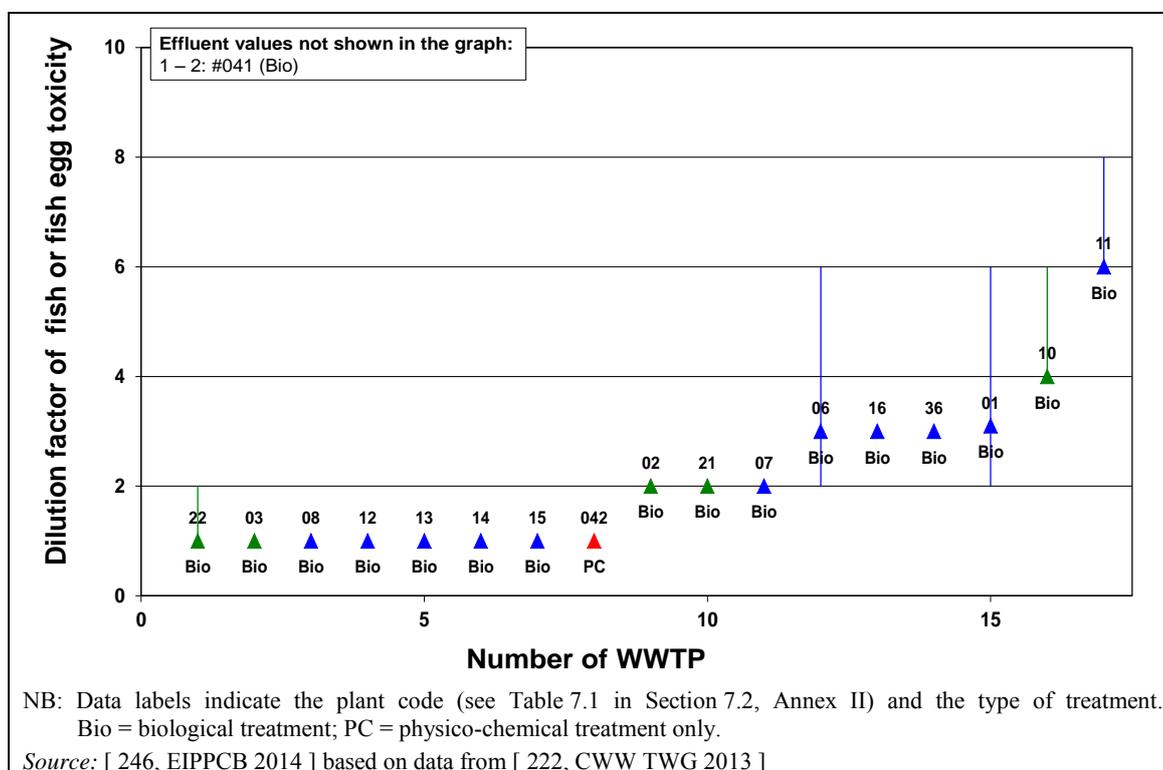
Figure 2.38: Fish or fish egg dilution factors in the effluents of directly discharging WWTPs

2.4.10.3 Daphnia toxicity

Overview of WWTP performance on daphnia toxicity
Data on toxicity were only gathered during the first survey, but not during the second. Out of a total of 52 directly discharging WWTPs participating in the first survey, toxicity values in the effluent were reported for 17 WWTPs (or 33 %) (Figure 2.39). Averaging periods are generally not indicated (yearly averages are indicated for two sites). Average values are based on a number of measurements spanning from 5 to 20.

NB: Data labels indicate the plant code (see Table 7.1 in Section 7.2, Annex II) and the type of treatment. Bio = biological treatment; PC = physico-chemical treatment only.
Source: [246, EIPPCB 2014] based on data from [222, CWW TWG 2013]
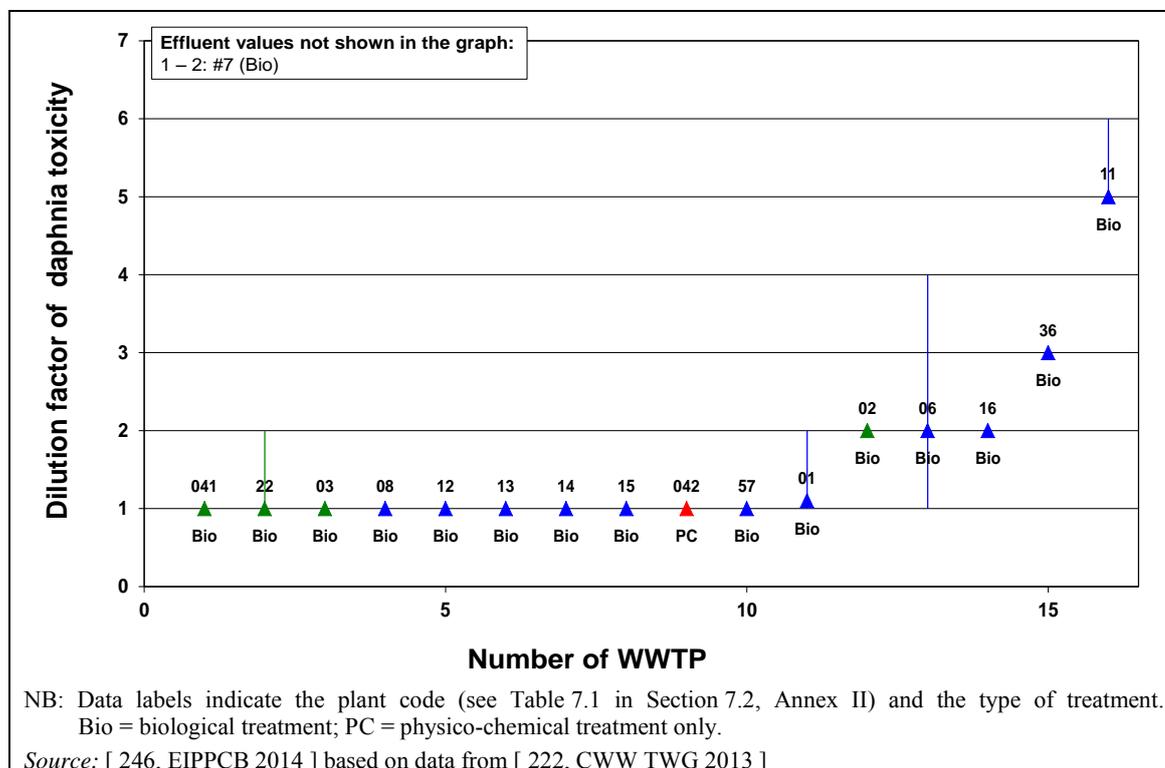
Figure 2.39: Daphnia dilution factors in the effluents of directly discharging WWTPs

2.4.10.4 Algae toxicity

Overview of WWTP performance on algae toxicity
Data on toxicity were only gathered during the first survey, but not during the second. Out of a total of 52 directly discharging WWTPs participating in the first survey, algae toxicity values in the effluent were reported for 16 WWTPs (or 31 %) (Figure 2.40). Averaging periods are generally not indicated (yearly averages are indicated for one site). The number of measurements span from 5 to 22.
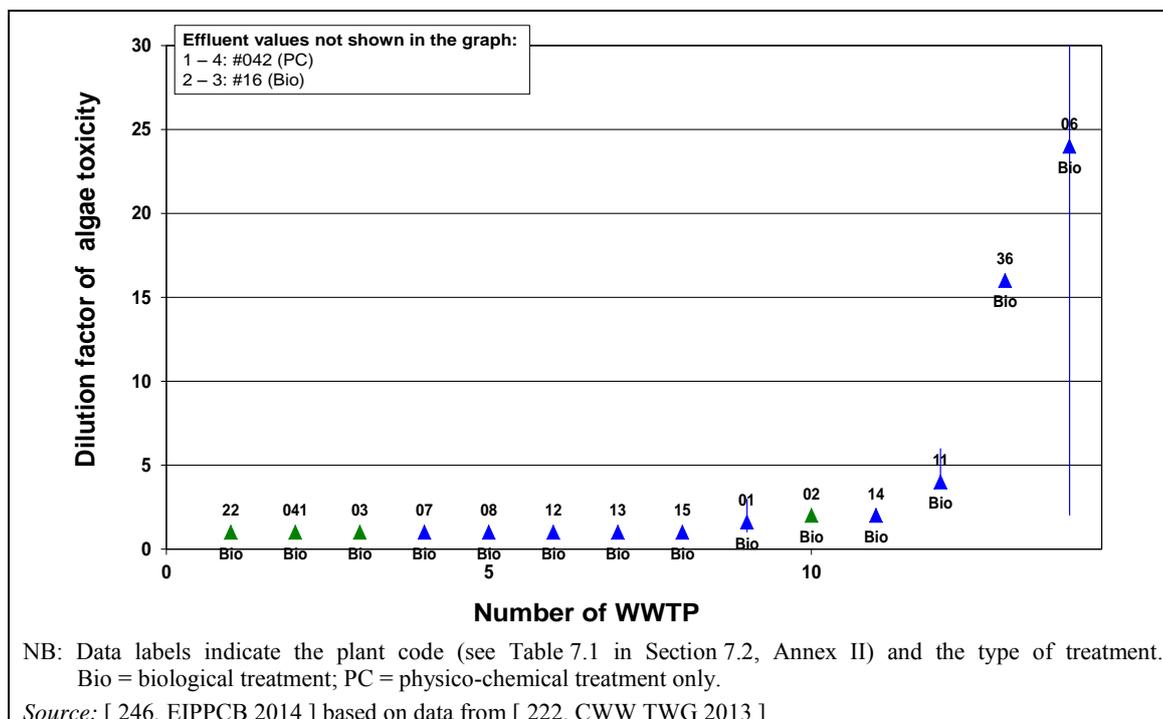
Figure 2.40: Algae dilution factors in the effluents of directly discharging WWTPs

2.4.10.5 Luminescent bacteria toxicity

Overview of WWTP performance on luminescent bacteria toxicity

Data on toxicity were only gathered during the first survey, but not during the second. Out of a total of 52 directly discharging WWTPs participating in the first survey, luminescent bacteria toxicity values in the effluent were reported for 18 WWTPs (or 35 %) (Figure 2.41). For installation #41, toxicity values were reported in Equitox/m^3 stemming from a commercial test. Conversion to dilution factors is not straightforward. Averaging periods are generally not indicated (yearly averages are indicated for two sites). Average values are based on a number of measurements spanning from 5 to 20.
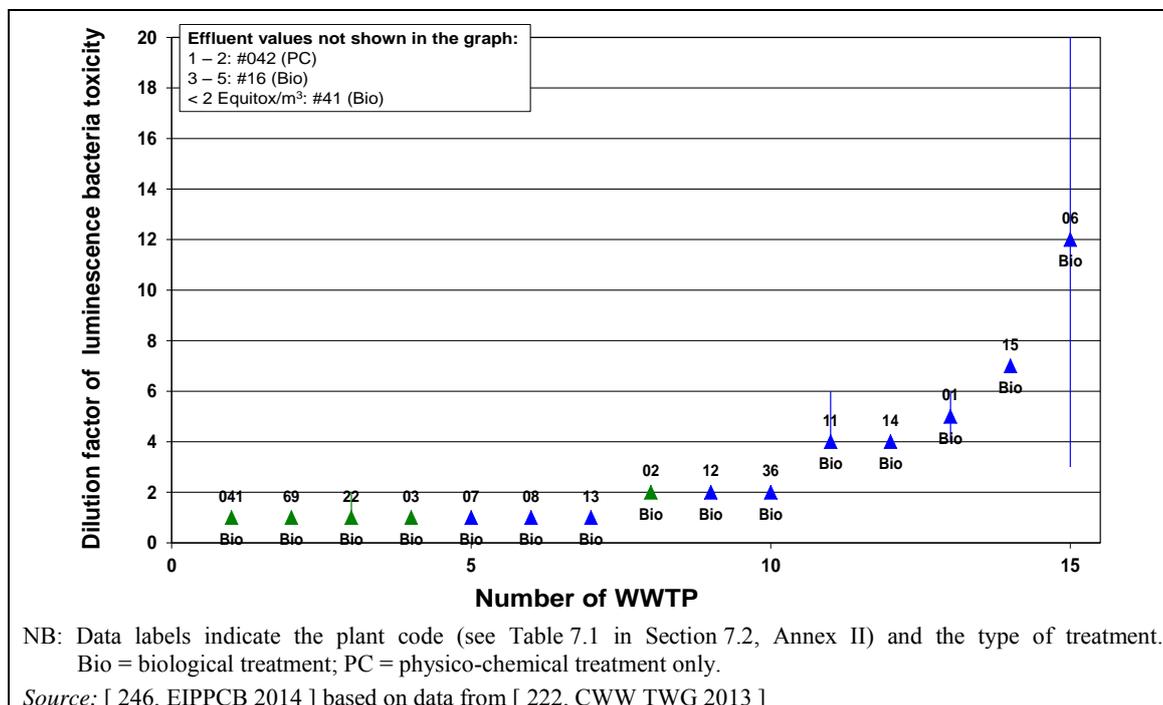
Figure 2.41: Luminescent bacteria dilution factors in the effluents of directly discharging WWTPs

3   TECHNIQUES TO CONSIDER IN THE DETERMINATION OF BAT

This chapter describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this document. The techniques described include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

The main focus of this chapter is on environmental management systems and end-of-pipe treatment techniques for waste water and waste gas. Other issues that are covered include monitoring of emissions, water usage and waste water generation, waste management, and sludge treatment. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations).

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter addresses these considerations. The standard structure in Table 3.1 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied in the sector. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

Table 3.1:   Information for each technique

Headings within the sections
Description
Achieved environmental benefits
Cross-media effects
Operational data
Applicability
Economics
Driving force for implementation
Example plants
Reference literature

3.1   Environmental management

3.1.1   Overview

Section 3.1 adds detail to the general descriptions in Chapter 1 and mostly describes the aspects of waste water and waste gas management in the context of the IED (2010/75/EU). 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 section describes environmental management as the interplay between management systems and management tools and is not restricted to waste water and waste gas issues, but to the involvement with the IED (2010/75/EU) 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 outline and the relevant tools to implement an environmental management system valid for chemical sites.

3.1.2   Environmental management systems (EMS)

Description
The Directive defines 'techniques' (under the definition of 'best available techniques') as 'both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned'.

In this respect, an environmental management system (EMS) is a technique allowing operators of installations to address environmental issues in a systematic and demonstrable way. EMSs are most effective and efficient where they form an inherent part of the overall management and operation of an installation.

An EMS focuses the attention of the operator on the environmental performance of the installation; in particular through the application of clear operating procedures for both normal and other than normal operating conditions, and by setting out the associated lines of responsibility.

All effective EMSs incorporate the concept of continuous improvement, meaning that environmental management is an ongoing process, not a project which eventually comes to an end. There are various process designs, but most EMSs are based on the plan-do-check-act cycle (which is widely used in other company management contexts). The cycle is a iterative dynamic model, where the completion of one cycle flows into the beginning of the next (see Figure 3.1).
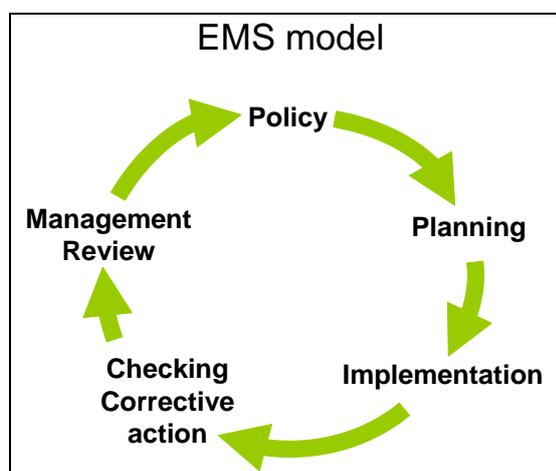
Figure 3.1: **Continuous improvement in an EMS model**

An EMS can take the form of a standardised or non-standardised ('customised') system. Implementation and adherence to an internationally accepted standardised system, such as EN ISO 14001:2015, can give higher credibility to the EMS especially when subjected to a properly performed external verification. EMAS provides additional credibility due to the interaction with the public through the environmental statement and the mechanism to ensure compliance with the applicable environmental legislation. However, non-standardised systems can, in principle, be equally effective provided that they are properly designed and implemented.

While both standardised systems (EN ISO 14001:2015 or EMAS) and non-standardised systems apply in principle to **organisations**, this document takes a narrower approach, not including all activities of an organisation, e.g. with regard to their products and services, due to the fact that the Directive only regulates **installations/plants**.

An EMS can contain the following components:

I.commitment of the management, including senior management;
II.an environmental policy that includes the continuous improvement of the installation by the management;
III.planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
IV.implementation of procedures paying particular attention to:

a)structure and responsibility,
b)recruitment, training, awareness and competence,
c)communication,
d)employee involvement,
e)documentation,
f)effective process control,
g)maintenance programmes,
h)emergency preparedness and response,
i)safeguarding compliance with environmental legislation;

V.   checking performance and taking corrective action paying particular attention to:

a)monitoring and measurement (see also the Reference Report on Monitoring of Emissions to Air and Water from IED installations) ([101, COM 2016]),
b)corrective and preventive action,
c)maintenance of records,
d)independent (where practicable) internal and external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;

VI.review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;

VII.preparation of a regular environmental statement;

VIII.validation by a certification body or an external EMS verifier;

IX.following the development of cleaner technologies;

X.consideration for the environmental impacts from the eventual decommissioning of the installation at the stage of designing a new plant, and throughout its operating life;

XI.application of sectoral benchmarking on a regular basis;

XII.waste management plan (see Section 3.4.1).

Specifically for the chemical industry sector, it is also important to consider the following potential features of the EMS:

XIII.on multi-operator installations/sites, establishment of a convention that sets out the roles, responsibilities and coordination of operating procedures of each plant operator in order to enhance the cooperation between the various operators (see Section 3.1.3);

XIV.establishment of inventories of waste water and waste gas streams (see Section 3.1.5.2.3).

In some cases, the following features are part of the EMS:

XV.odour management plan (see Section 3.5.5.2);

XVI.noise management plan.

Achieved environmental benefits
An EMS promotes and supports the continuous improvement of the environmental performance of the installation. If the installation already has a good overall environmental performance, an EMS helps the operator to maintain the high performance level.

Operational data
No information provided.

Cross-media effects
None reported. The systematic analysis of the initial environmental impacts and scope for improvements in the context of the EMS sets the basis for assessing the best solutions for all environmental media.

Applicability
The components described above can typically be applied to all installations within the scope of this document. The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

Economics
It is difficult to determine accurately the costs and economic benefits of introducing and maintaining a good EMS. There are also economic benefits that are the result of using an EMS and these vary widely from sector to sector.

External costs relating to verification of the system can be estimated from guidance issued by the International Accreditation Forum [170, IAF 2010].

Driving forces for implementation
The driving forces for the implementation of an EMS include:

- improved environmental performance;
- improved insight into the environmental aspects of the company which can be used to fulfil the environmental requirements of customers, regulatory authorities, banks, insurance companies or other stakeholders (e.g. people living or working in the vicinity of the installation);
- improved basis for decision-making;
- improved motivation of personnel (e.g. managers can have confidence that environmental impacts are controlled and employees can feel that they are working for an environmentally responsible company);
- additional opportunities for reduction of operating costs and improvement of product quality;
- improved company image;
- reduced liability, insurance and non-compliance costs.

Example plants
EMSs are applied in many chemical installations throughout the EU.

Reference literature
[101, COM 2016] [170, IAF 2010] [172, CEN 2015] [173, Reg. 1221/2009]

3.1.3   Conventions

Description
A 'convention' is a contractual document dealing directly or indirectly with environment, health and safety (EHS) risks, and established between two or more operators/owners of installations operating on the same industrial site. Contracts between a company and its subcontractors are not considered here (in Europe, these relationships are covered by occupational health and safety regulations in terms of risk prevention, e.g. Directive 89/391/EEC on the introduction of measures to encourage improvements in the safety and health of workers at work [84, Directive 89/391/EEC 1989]).

Conventions generally aim, among other things, at:

- clarifying the role, responsibilities, and coordination of operating procedures of each operator/owner of an installation on the industrial site and other parties of the convention regarding shared (or linked) infrastructures, installations, activities and associated resources (this could also include landowners and entities responsible for past pollution of the site) in order to enhance the cooperation between the various operators;
- defining the rules of use and the financing of shared infrastructures, installations or activities;
- identifying and minimising the risks of one operator's activities that could have a negative impact on another operator's employees or installations and the overall risks at the level of the whole site (including environmental risks);
- defining common EHS rules applicable at the level of the whole site (e.g. internal emergency plans to deal with accidents and possible domino effects, waste management, operation of common waste water/waste gas treatment plants, and the monitoring of fugitive/diffuse emissions).

A convention is often considered a guarantee for an operator with respect to the continued operation of shared infrastructures (e.g. pipe networks, sewers, roads, fences, fire protection systems), facilities (e.g. common waste water/waste gas treatment plant, power plant, industrial gas supplies, warehouses and chemical storage) and services (e.g. security and training).

An efficient convention system generally contains the following elements:

- Decision-making bodies (committees) whose responsibilities encompass:

    ◦ shared resources (e.g. short/long-term financing, operation and maintenance);
    ◦ common EHS rules (e.g. definition, implementation, control and updating).
    The weight of each operator in decision-making is not only based on the financial aspects and payroll; potential hazards and real impacts of the activities (especially on the environment) are taken into account. The decision-making bodies set their own rules including procedures for resolving possible disagreements or conflicts and confidentiality/proprietary issues.

- Use of an 'infrastructure company' with clearly stated roles and authority regarding the global interest of the site to:

    ◦ operate and maintain shared resources (e.g. pipe networks, roads, sewers, power supplies);
    ◦ provide common services to the other operators (e.g. site access authorisations, general training of subcontractors before they enter the site, traffic rules, and whole site emergency procedures);
    ◦ coordinate activities of operators for EHS activities relative to the whole site.

- Checking processes (e.g. audits) to assess how operators comply with the terms of the convention. This includes how to deal with non-conformities. Checks or audits can be carried out by the 'infrastructure company' as well as by companies completely external to the industrial site.

When the convention deals with the operation of a common waste water or waste gas treatment plant, the convention can, in particular, define the spectrum of waste waters or waste gases that the common treatment plant is able to treat under normal operating conditions (e.g. for a WWTP, the load of pollutants in kg/d as a monthly average, maximum load of pollutants in kg/d over five consecutive days, see Section 3.1.5.2.3).

Achieved environmental benefits
Enhanced cooperation between the various operators of a large industrial site on EHS issues is expected to bring about environmental benefits such as reduced raw material and energy consumption, lower emissions to air and water, enhanced capability and efficiency to respond to emergency situations and the prevention or minimisation of environmental damage.

Cross-media effects
None.

Operational data
Conventions concentrate on the definitions and rules of the exercise of individual and collective responsibilities.

The term 'convention' refers to operational documents rather than including them.

Conventions state that rules are linked to installations and not to operators (a new operator who purchases an existing installation on the site has to sign the convention).

Conventions define rules as to how they should be updated. Updating of conventions can be made for example every five years.

Applicability
Conventions are applicable at industrial sites where more than one operator is carrying out production activities if there are risks at the interface level of their activities.

Economics
Conventions have several positive economic aspects that derive from, for example, the efficient management (including the protection from damage) of shared infrastructures/installations (e.g. central WWTP), and the faster and more efficient response to events impacting the site, thus limiting financial risks.

Driving force for implementation
On the side of the individual operator, establishing a convention is considered to increase the efficiency of operation by doing the following:

- clearly defining the responsibilities of each operator;
- having guarantees concerning the long-term management of efficiently shared resources;
- sharing practices, vocabulary and a culture of risk with other operators.

Competent authorities can encourage the establishment of conventions as a way to clarify the responsibilities of the different companies in large chemical sites with respect to the overall management of a site and to grasp the positive aspects with regard to the protection of the environment.

Example plants
- Les Roches chemical site, Roussillon, France.
- Lavéra petrochemical site, Lavéra, France.
- Villers Saint-Paul chemical platform, Villers Saint-Paul, France [149, ATOFINA et al. 2003].

Reference literature
[84, Directive 89/391/EEC 1989] [120, Gaucher and Dolladille 2008] [149, ATOFINA et al. 2003]

3.1.4   Waste water management

Description
Many chemical sites operate a central WWTP as final treatment step. In most cases, such final treatment is based on biological treatment, but sometimes only physico-chemical treatment is used.

Operating procedures
The operation of a central WWTP is governed by operating procedures linked to the procedures/EMS (see Section 3.1.2) of the individual plants/units from which the waste waters originate. These procedures describe in particular the necessary interactions between the operators of the individual installations producing the waste waters and the central WWTP operators. When operators of the individual installations and operators of the central WWTP pertain to different companies, conventions are set up (see Section 3.1.3). Adequate communication between the production plants and the central WWTP must be ensured (e.g. radio, mobile phone, PC network) for normal operations and incidental or emergency situations.

All plants/units or even areas of the chemical site have local emergency procedures for ensuring that leaks of harmful substances are appropriately dealt with; this generally involves containing the release in sumps or intermediate bulk containers (IBC) and notifying the environmental section so that they can assess these waste water streams for disposal on or off site.

Managing fluctuations
The operators of a central WWTP have to manage the fluctuations of the influent to the central WWTP to cope with the seasonal variations (summer/winter), start-up and shutdown procedures, Cleaning-In-Place (CIP), continuous and/or batch operations, seasonal campaign

productions (e.g. fine chemicals) and other conditions that can affect the composition of the influent (see also Section 3.3.2.1).

When the production of chemicals is organised in campaigns (e.g. in the production of fine organic or inorganic chemicals), procedures are in place to evaluate the impact of the production changes on the waste water streams sent to the sewer to optimise the use of the central WWTP and to minimise the impact on the environment. Process water effluents are analysed routinely from campaigns to check for similarity. Changes to the monitoring strategy/procedures/equipment may be needed if the production (e.g. process, equipment, product) is modified (see also Section 3.1.5.3.2).

As a result of all the possible operational issues that might affect the quality and/or the quantity of the influent waste water to the central WWTP, its operators will observe a wide range of emissions for many different parameters. In order to optimise the performance of the WWTP with the changing influent conditions, information is needed on the limitations of the WWTP design (e.g. hydraulic capacity, type of aeration, aerobic and/or anaerobic treatment steps), the interference to the biological community/biocoenosis and the local operating conditions.

Knowledge of the individual waste water streams to be treated
Effective waste water management on a large chemical site requires knowledge of the relevant parameters in the local situation, e.g. mass flows, concentrations of specific single substances or sum parameters, temperature, pH, as well as flexibility in handling different circumstances and relations between different waste water streams coming from the production plants/units. Establishing and maintaining a stream inventory/register (see Section 3.1.5.2.3) allows for identifying the parameters that can have an influence on the performance of the central WWTP and to take all the necessary actions in order to ensure its proper functioning.

For each waste water effluent sent to the central WWTP, the operator of the central WWTP and the operator of the plant/unit from which the effluent originates collaborate to set up waste water specifications which define, in particular, the range of each relevant parameter for the effluent (e.g. flow rate, pH, temperature, biodegradability and bioeliminability, solid content, toxicity to biomass and to the aquatic environment, heavy metals, colour) as well as the nature and frequency of the monitoring regime for the effluent.

As long as the waste water quality is within specification, it can generally be discharged to the sewer system without further communication between the operators of the plant/unit and the operators of the central WWTP. When the water effluent is off-specification and this is identified, the operators of the plant/unit from which the effluent originates contact the operators of the central WWTP in order to decide how to handle this new situation. Waste water may be sent to the sewer without any pretreatment, if the treatment capacity of the central WWTP allows for it (in terms of the nature and amount of the waste water capable of being treated for the specific situation). In any other case, waste water is temporarily stored in buffer tanks or emergency storage basins. The emergency basins can serve as buffers to regulate the input to the sewer in order to remain within the capacity of the WWTP. In the emergency storage basins, pretreatment is feasible.

Testing waste waters before decision for treatment
Before new waste water conditions are accepted for it to be discharged to the sewer network of the site, they need to be examined and/or tested. Tests are carried out under the supervision of analytical experts from the WWTP and in representative conditions with the original waste water from the actual central WWTP. The effluent is tested including using biotests, if needed (e.g. a Zahn-Wellens test can be used). If the new waste water cannot be accepted, pretreatment may be needed or disposal will be required.

Monitoring of the sewer network of the chemical site
An effective waste water management system necessitates an appropriate waste water monitoring system on the site. This does not mean to monitor each parameter at each sewer junction but to effectively define the relevant monitoring points, monitoring parameters and

monitoring frequencies (e.g. continuous, grab sampling) for an efficient waste water management.

Some examples of important parameters to be monitored include:

- the mass flow of waste water;
- the temperature of waste water;
- carbon, nitrogen and phosphorus and the relationship between these parameters in the aeration step of the central biological WWTP;
- pH;
- critical (single) substances from single plants/units;
- sludge activity (temperature, feed concentration, retention time) in biological WWTPs.

Achieved environmental benefits
Optimised performance of the central WWTP, avoidance of poor environmental performance as a result of fluctuations in the quality and/or quantity of the influent to the central WWTP.

Cross-media effects
None.

Operational data
The treatment process of a central biological WWTP consists of mixed microbial communities which are able to degrade the pollutants under certain operating conditions. In order not to deteriorate the performance of the biological treatment process, the operators of the WWTP have to make sure that the operating requirements are met at all times. In case of disturbances to the performance of the biological treatment, the operators have to take necessary actions to manage the specific situation efficiently and in a timely manner. As a minimum requirement, the C/N/P ratio in the influent has to be ensured under all operating conditions. Therefore, the operators of the WWTP have to have information on the influent waste waters and on the operation of pretreatment units inside the chemical plants. In case of the lack of a carbon source for denitrification and/or the nutrients (N, P), the operators should supply a feed (e.g. side products, concentrated waste water stream) to compensate for the deficient amount. With respect to maintaining the C ratio in the central WWTP, different wastes containing a carbon source can be used, and therefore, the degradability of the waste substances in the biological treatment determines whether or not it can be used as feed.

In order to ensure a good performance for the biological treatment of the biological WWTP, the C/N/P ratio, sludge age, structure of sludge flocs, adaptation time to variation of influents, toxic and/or inhibitory influence should be kept under control.

If a pretreatment unit (e.g. distillation unit) for reducing ammonia nitrogen (NH_4-N) is installed and operated in a chemical plant/unit in a situation where the central biological WWTP may need TKN (C/N/P ratio), the operator of the central WWTP may ask to not operate the pretreatment unit and send the ammonia-rich waste water to the sewer system. In that case, the central WWTP does not need to use additional nutrients, e.g. urea or HNO_3, the operator of the chemical plant/unit saves energy for the pretreatment of waste water, and no waste is generated. A high concentration of nitrogen in the single waste water stream can be allowed if the mass flow is balanced within the whole waste water influent and homogenised in the buffer before aeration (WWTP #21) [222, CWW TWG 2013].

Waste water from the blowdown of closed cooling circuits which contain phosphorus may be discharged to the central biological WWTP for the same reason (C/N/P ratio). The use of an additional feed, e.g. of H_3PO_4, may be avoided and the direct discharge of phosphorus to the receiving water body is reduced (WWTP #21) [222, CWW TWG 2013].

Dealing with non-routine waste water arisings
Non-routine waste water arisings (i.e. side products, failed production runs, etc.) are assessed by the environmental section for release to the sewer, based on information that includes:

- health and safety data (to protect plant personnel, especially those working in the central WWTP and on the sewer network);
- aquatic toxicity data;
- biodegradability/bioelimination data of each waste water stream;
- odour threshold;
- the removal efficiency of the central WWTP.

Waste streams are only released to the sewer when it can be shown that the central waste water treatment processes of the site can cope with the discharge. If there is any doubt, waste water streams are sent off site for disposal or to temporary storage for verification before a decision on treatment is made.

Applicability
Applicable to all chemical sites discharging to a central WWTP.

Economics
No information provided.

Driving force for implementation
Efficient waste water management.

Example plants
WWTP #21 [222, CWW TWG 2013].

Reference literature
[222, CWW TWG 2013] [227, CWW TWG 2009]

3.1.5   Management tools

3.1.5.1   Overview

To operate an EMS around the loop of strategic items (see Figure 3.1), several kinds of (management and engineering) tools are used. These can be roughly categorised as:

- inventory management 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 (see Section 3.1.5.2);
- operational management tools, helping to decide upon planning, designing, installing, operating and improving pollution prevention and/or treatment facilities (see Section 3.1.5.3);
- strategic management tools, including the organisation and operation of release handling on the entire chemical site in an integrated manner (see Section 3.1.5.4);
- safety and emergency tools, necessary for troubleshooting in the case of unplanned events (see Section 3.1.5.5).

3.1.5.2 Inventory management tools

3.1.5.2.1 Overview

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;
- the characteristics of the pollutants of the individual production processes;
- the characteristics of the emitted streams;
- local factors.

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 to reduce the necessary parameters (e.g. number of measurements) without relevant loss of information can normally be found.

3.1.5.2.2 Site inventory

Description
A site inventory consists of information on:

- geographical location of the installation/site and production units (map and plot plan);
- climate, geography, quality of the soil and groundwater, neighbourhood, and receiving water;
- size of the site (total area, built-up area, drained area, covered area);
- number of employees;
- production units;
- list of production plants including, for each one, data on:

  ◦ the classification of production plants according to the IED (2010/75/EU), Annex I, 4. Chemical Industry, Sections 4.1–4.6 [5, Directive 2010/75/EU 2010],
  ◦ typical production plant data;

- information on the production processes, for each process, including:

  ◦ 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);

- sewer system (sewer, WWTP, rainwater drainage).

Achieved environmental benefits
A site inventory is a tool that is expected to help plant management react more effectively and more quickly to environmental challenges. A site inventory will help in the determination and ranking of the significance of the environmental impacts of the site and in the implementation of an effective EMS to address them (see Section 3.1.2).

Cross-media effects
There are no cross-media effects associated with a site inventory.

Operational data
No information provided.

Applicability
The technique is applicable to new and existing installations.

Economics
No information provided.

Driving force for implementation
Improving the environmental management system is the main driving force for the implementation of the technique.

Example plants
No information provided.

Reference literature
[5, Directive 2010/75/EU 2010]

3.1.5.2.3   Stream inventory/register

Description
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/register (waste water inventory/register, waste gas inventory/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 possibilities of reduction at the source. The sources of waste water are listed in Section 1.4.2; those for waste gas in Section 1.4.3. Stream inventories/registers form the basis for waste water segregation and pretreatment strategies (see Sections 3.1.5.3.4.2 and 3.1.5.3.5.2).

When waste waters are further treated in a central WWTP, establishing and maintaining a stream inventory/register allows for identifying the pollutants/parameters that can have an influence on the performance of the central WWTP and to take all necessary actions in order to ensure the proper functioning of the WWTP. In this context, a stream inventory/register is a technique used in the framework of conventions (see Section 3.1.3).

A stream inventory/register addresses the following aspects, if relevant to the particular local conditions:

- information about the chemical production process, such as:

  ◦ chemical reaction equations including starting compounds, products and side 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;
  ◦ description of process-integrated techniques and waste water/waste gas treatment at source including their performances;

- information, as comprehensive as is reasonably possible, about the characteristics of the streams, such as:

  ◦ data on concentrations and loads of relevant pollutants/parameters 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);
  ◦ explosive limits (lower explosive limit (LEL) and higher explosive limit (HEL));
  ◦ reactivity (for waste gas);
  ◦ relevant contaminants and/or parameters, such as:
    ▪ COD/TOC, NH_4-N, NO_3-N and NO_2-N, phosphorus, heavy metals, halogenated hydrocarbons, persistent organic pollutants – 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 (VOCs) 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 issues, such as oxygen, nitrogen, water vapour, and/or dust.

The purpose of a stream inventory/register 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 including:

- 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 mass balance(s), the extent of which would depend on several factors (e.g. type of pollutant, frequency of emissions).

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/register and an attractive basis for identification of further release reduction potential, the respective streams at the top of each ranking list being prime candidates for more 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.

Achieved environmental benefits
Achieved environmental benefits include the reduction of emissions to water and/or air. Identification of relevant waste water/waste gas streams is a prerequisite for an efficient waste water/waste gas management and for the reduction of emissions by technical and management measures.

Cross-media effects
There are no cross-media effects associated with this technique.

Operational data
At a large chemical site in Germany (about 30 different companies and 100 production plants), the waste water register includes an assessment of all relevant point sources at the different process steps. In this example site, since the organic content at the outlet of the final treatment is relatively low (COD < 75 mg/l) and the waste water effluent does not pose toxicity problems, the waste water register is less detailed and contains 1–15 waste water streams per production unit, depending on the diversity of the waste water arisings. The authorities receive updated data every three years or when major changes are implemented [134, LANUV NRW 2008].

The waste water register includes an assessment of the waste water volume and pollutant concentrations/loads at the different sources. It includes average data for the respective year on waste water volume and load and concentrations of TOC, AOX, as well as the most common heavy metals (i.e. Hg, Cd, Cu, Ni, Pb, Cr, Sn, Zn) and main compounds known to be present in the waste water (e.g. BTEX, organic products, salts, nitrogen compounds as total nitrogen) coming from the different sources. An additional issue is priority pollutants. Findings of the example plant are discussed in [134, LANUV NRW 2008].

The register also includes the results of a systematic assessment on the feasibility of potential production-integrated measures to avoid waste water and/or to reduce loads (see Section 3.3).

An example of the basic data on the composition and quantity of waste waters from a multi-purpose plant can be found in the OFC BREF [105, COM 2006].

Applicability
The technique is generally applicable.

Economics
No information provided.

Driving force for implementation
Inventories/registers may be used to assess the implementation of BAT and may constitute basic information for authorities in order to set emission limit values for the total loads on the basis of balancing models [134, LANUV NRW 2008].

Example plants
Marl chemical park, North Rhine-Westphalia, Germany [134, LANUV NRW 2008].

Reference literature
[105, COM 2006] [134, LANUV NRW 2008]

3.1.5.2.4 Mass balances

Description
Mass balances are one basis for understanding the processes on a site and the development of improvement strategies. For a complete mass balance, the inputs must equal the outputs. Table 3.2 shows the typical elements of a mass balance. Not every output path is relevant in every case (e.g. heavy metals cannot be destroyed).

Table 3.2: Typical elements of a mass balance

Input	Output
- Withdrawal from stock - Purchases - Production - Recycling/reuse from other processes	- Deposit in stock - Consumption - Destruction - Recycling/reuse to other processes - Losses to air - Losses to water - Disposal

A solvent management plan according to Part 7 of Annex VIII to the IED (2010/75/EU) constitutes an example of a mass balance [5, Directive 2010/75/EU 2010].

Achieved environmental benefits
Mass balances are essential for understanding on-site processes and the development of improvement strategies.

Cross-media effects
There are no cross-media effects.

Operational data
An example of a water balance for the production of fertilisers is given in the LVIC-AAF BREF [102, COM 2007].

Mercury balances are a frequently used tool in mercury-cell chlor-alkali plants [110, COM 2014] [124, Euro Chlor 2010].

Applicability
This technique can in some cases provide useful insights into a process. Mass balances are very time-consuming and this is a limitation to their use. Mass balances are generally not sufficiently accurate to quantify emissions from a chemical plant.

Economics
Additional measurements are required (hence costs) and, therefore, additional staff are needed.

Driving force for implementation
The driving forces for implementation of the technique are reporting requirements imposed by authorities as well as the development of improvement strategies to reduce pollution.

Example plants
Mercury-cell chlor-alkali plants.

Reference literature
[5, Directive 2010/75/EU 2010] [102, COM 2007] [110, COM 2014] [124, Euro Chlor 2010]

3.1.5.3   Operational management tools

3.1.5.3.1   Overview

While the inventory management tools (see Section 3.1.5.2) 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.

3.1.5.3.2   Management of changes involving process and/or plant modifications

Description
Changes involving process and/or plant modifications are relatively frequent in the chemical industry sector, e.g. to improve the performance/efficiency of production, to enhance safety or security, to enable the manufacture of new or modified products, to reduce maintenance or operating costs, and to enhance environmental protection. In addition, changes are carried out in order to satisfy market strategies that may involve changes of product grade and/or the reallocation of production and consequently the transfer of processes to other installations/plants. Changes are also conducted in the framework of decommissioning the plant.

Modifications can be classified as minor or major, or as substantial or not, generally based on the following criteria:

- the foreseen impact of the changes on the safety of the installation including both processes and workplace safety issues;
- the likely impact of the changes on the environment (air, water, waste, energy and raw material consumption);
- the extent and complexity of the changes.

According to the IED (2010/75/EU), substantial changes within an IED plant or installation are subject to the granting of prior authorisation by the competent authority [5, Directive 2010/75/EU 2010].

Plant modifications are designed and implemented with the objective of maintaining the installations in compliance with laws, regulations and standards (both internal and industry standards), to protect the environment and to ensure an appropriate level of reliability and safety of the operation of the plant.

Whole effluent assessment (WEA, see Section 3.2.2.3) is an instrument that is used in some Member States (e.g. Sweden) in the permitting procedure for checking that the implementation of process changes does not harm the environment.

Management procedures concerning plant modifications are in place as part of the EMS to manage plant modifications (see Section 3.1.2, point 'c'). An effective management of changes is generally achieved by the implementation and follow-up of appropriate procedures to verify and control the projected modifications from the very early phase of the investment planning.

Changes involving process and/or plant modifications take into account organisational aspects as well as human factor aspects, especially when the changes are considered major based on the criteria mentioned above.

A sample workflow for the management of changes is given in Figure 3.2.

MANAGEMENT OF CHANGES – SAMPLE WORKFLOW

PLANNED MODIFICATION(S), e.g.:
• PROCESS (NEW, TRANSFER)
• PLANT, EQUIPMENT
• RAW MATERIAL(S) (QUANTITY, QUALITY)

ENGINEERING/MAINTENANCE SAFETY/ENV. PROTECTION

ANALYSIS & EVALUATION

SITE/PLANT MANAGEMENT R&D/PROCESS DEVELOPMENT

Additional requirements, modifications, reviews

(Process risk assessment)
(Workplace risk assessment)
ENVIRONMENTAL ASSESSMENT

Additional requirements, modifications, reviews

Compliance issues, e.g.
IPPC permit, SEVESO updates, ATEX/fire permits, pecific local requirements

Waste gas treatment
Waste water treatment
Waste management

OHS issues, e.g.
standard operating procedures, emergency procedures, sanitary surveillance, training

PERMIT(S)

INSTALLATION(S)

ORGANISATION SET-UP

Scale up/trials/start-up
ormal operations

Figure 3.2: Sample workflow for the management of changes

Achieved environmental benefits
An adequate management of changes minimises the environmental impact of carrying out plant modifications.

Cross-media effects
No cross-media effects are believed to be likely.

Operational data
Examples of plant modifications or changes are provided in the following list (the list is not exhaustive):

- the installation/decommissioning of machinery/equipment (e.g. pump, heat exchanger, filter, valve, instrumentation, storage tank, vessel);
- the modification of connections between plants/processes/systems/components;
- the modification of set-up parameters of the process safety control equipment (e.g. set-up pressure of safety valves, rupture disks, pressure, temperature and level metering devices);
- the modification of logical loops (mode of intervention of instrumentation);
- the substitution of machinery/equipment for different alternatives;
- the repair of machinery/equipment whenever the intervention leads to relevant modifications of the characteristics and/or performances (e.g. repair of a stirrer with modification of typology, repair of a pump leading to significantly different performance characteristics).

Examples of changes which are not generally considered to be relevant modifications are listed below:

- the substitution of machinery/equipment for identical ones or those with the same characteristics;
- the repair of machinery/equipment keeping the same performance characteristics;
- the interventions of ordinary, extraordinary, programmed and preventive maintenance without modification of the original characteristics of the machinery/equipment being maintained.

Applicability
The management of changes is applicable at all installations. The extent to which management procedures to deal with plant modifications are developed depend for the most part on the size and nature of the operation (i.e. procedures in place at large Seveso plants are expected to be more developed than those in place at small non-Seveso installations).

Economics
No relevant extra costs are expected. Costs savings are expected.

Driving force for implementation
The drivers for implementation include minimising the environmental impact and complying with legislation.

Example plants
Several IED installations, in particular Seveso plants.

Reference literature
[5, Directive 2010/75/EU 2010] [156, Grandi 2008]

3.1.5.3.3   Setting and regular review of internal targets or programmes

Description
An EMS (see Section 3.1.2) 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. the 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.

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 improvements;

- 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 reduce 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 the 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.

Achieved environmental benefits
The technique is expected to help plant management react more effectively and more quickly to environmental challenges and therefore to minimise the impact of the functioning of the installation on the environment as a whole.

Cross-media effects
There are no cross-media effects associated with this technique.

Operational data

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 or environmental quality standards as well as technology standards and 'good manufacturing practice';
- the general requirements for river basin quality (Water Framework Directive [28, Directive 2000/60/EC 2000] 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 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:

  ○ fish test: LID = 2;
  ○ daphnia test: LID = 4;
  ○ algae test LID = 8;
  ○ luminescent bacteria test: LID = 16;
  ○ mutagenicity: LID = 1.5.

  The toxicity is expressed as 'dilution factors'. LID = 2 means that the waste water stream has to be diluted to half of its original concentration so that no toxic effects can be observed. See also Section 3.2.2.2.

As a long-term target for the future, the German chemical industry (according to the VCI declaration of May 2000 [93, VCI 2000]) aims to further reduce the toxic impact of its waste water discharge, taking into consideration:

- acute toxicity to fish, daphnia and bacteria;
- chronic toxicity to algae;
- mutagenicity.

They finally seek to ensure that their effluents into receiving water bodies do not exceed dilution factors of LID = 2 (for mutagenicity: LID = 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 ecotoxic effects (see Section 3.2.2.2).

The role of monitoring in target setting is mentioned in Section 3.2.2.1.

Applicability
The technique is generally applicable to new and existing installations.

Economics
No information provided.

Driving force for implementation
Improving the environmental management system is the main driving force for the implementation of the technique.

Example plants
No information provided.

Reference literature
[28, Directive 2000/60/EC 2000] [93, VCI 2000]

3.1.5.3.4   Selection of treatment options

3.1.5.3.4.1   Overview

With the necessary information concerning emissions arising on a chemical site and the environmental targets and demands defined, the next step is the selection of appropriate treatment 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 (e.g. vapour, oil),
  ◦ temperature,
  ◦ pressure;
- the load of the streams that need treatment;
- the targets 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/register (see Section 3.1.5.2.3) – always results in the need for additional site-specific conclusions to be taken into account, the key factors varying from site to site, by 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 lifetime;
- potential and degree of process integration within an installation and between installations;
- type and quality of the receiving medium;
- impact on the environment as a result of an actual or foreseen emission;
- remaining lifetime 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 analyses (water consumption, waste generation, energy consumption);
- investment and operating costs.

When 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 3.1.5.3.4.2 and 3.1.5.3.4.3 respectively.

3.1.5.3.4.2   Selection of waste water control system

Figure 3.3 illustrates a decision path for finding the appropriate waste water treatment system for the individual waste water streams.

The following questions, which contain the main objectives of the IED (2010/75/EU) – prevention, minimisation and control of pollution – 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 as a whole 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?

NB: Dotted lines symbolise alternative options.
Source: [251, Ullmann's 2000]
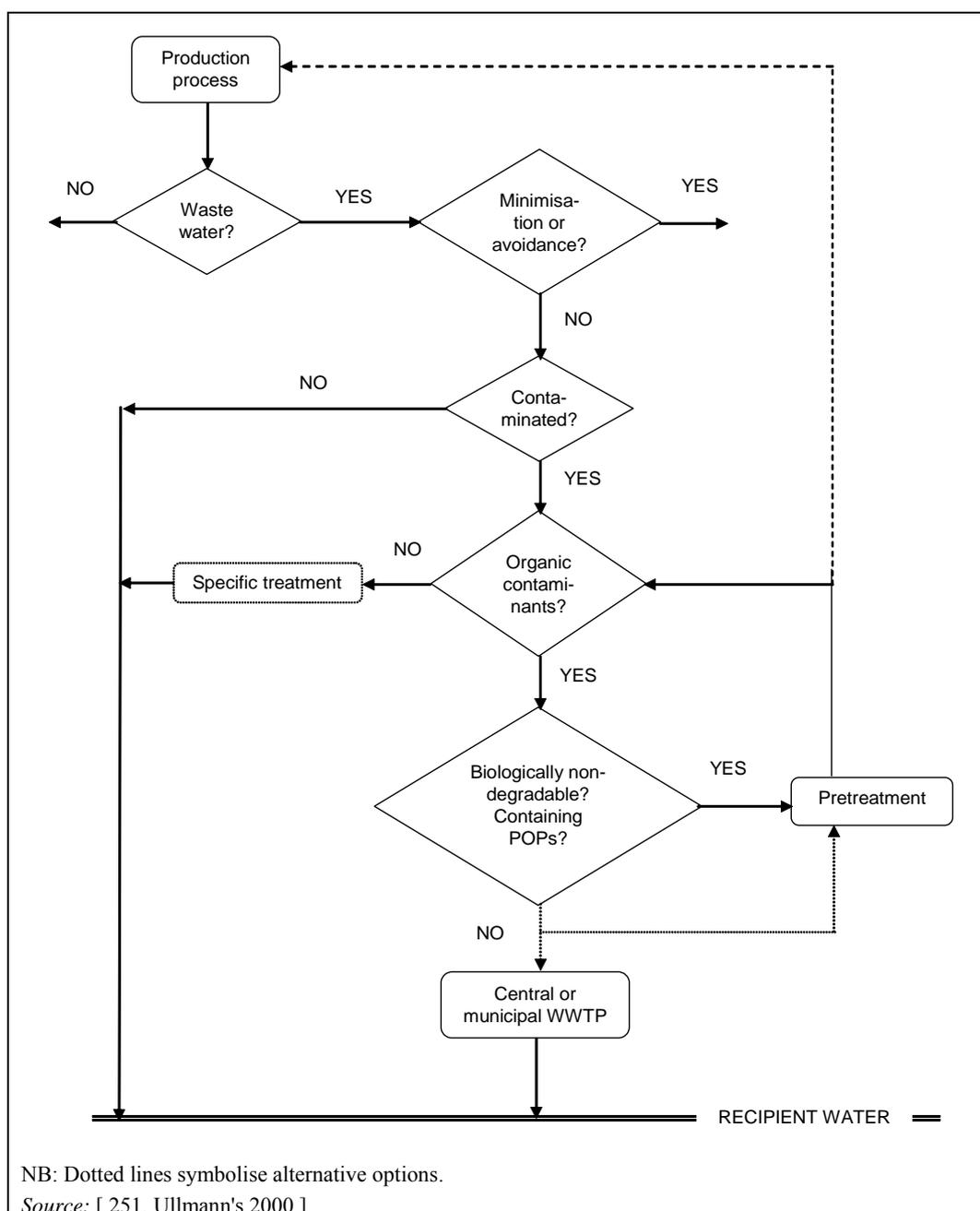
Figure 3.3:   Decision diagram for selecting an appropriate waste water treatment system

As an example criterion for prioritising a more thorough examination of tributary waste water streams, the presence of a refractory 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, priority substances and toxicity.

The selection procedure follows the steps mentioned in Section 3.1.5.3.4:

Source reduction
The options for waste water reduction at the source should be considered first. In many instances, these will result from process considerations described in the other chemical BREFs. Suggestions for frequently occurring causes of contamination are described below, categorised into subheadings.

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

- process water should be segregated from rainwater and other water effluent, to allow reuse or recycling, as well as to minimise the amount of waste water which requires treatment, the installation of a roof over certain process areas, loading and unloading bays, etc.;
- process water should be used in a recycle mode, whenever it is economically feasible, with a maximum number of recycles before discharge;
- direct contact cooling systems should be avoided whenever feasible;
- a critical review of the need for water scrubbing systems or, when they are used, an investigation into the potential for water regeneration and reuse (see Section 3.3.1) should be carried out;
- 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, should be minimised;
- free oil should be removed to a slop oil system before its discharge to the sewer;
- an effective water/hydrocarbon separation should be carried out as far as practicable in the process equipment before discharging the water to the sewer;
- if feasible, a process fluid should be used instead of steam in Venturi jet devices, or a liquid ring pump should be used, preferably using a process fluid as seal liquid (see Section 3.3.1.7), or a dry vacuum pump should be used, to minimise the contamination generated by vacuum devices;
- as far as possible, the discharge from safety valves, thermal relief valves, bleeds from double block isolation or twin seal valves should be captured, because it is not recommendable to discharge them to areas where clean rainwater is collected;
- laboratory effluent should be collected 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 measures should be taken into account:

- vents and drains should be plugged or capped whenever they are not in use;
- flush collection should be allowed in a slop system rather than sending 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;
- overfilling of vessels or tanks should be avoided by installation of an adequate level of instrumentation or adequate procedures;
- the use of hoses should be minimised;
- facilities to collect hose drips should be considered;
- roofs over loading racks should be considered;
- kerbs should be installed to ensure containment of spills;
- adequate instrumentation should be considered to protect against overfilling of road tankers;
- product loss should be avoided during water draw-off from tank bottoms;
- the installation of reliable interface detection instruments (i.e. to determine the position of a liquid/liquid or liquid/vapour interface in a remote inaccessible location) should be considered;
- the pigging of lines should be considered instead of flushing and draining, whenever applicable;
- spills should be vacuum cleaned whenever possible rather than hydrojetting or steaming them to the sewer;
- water hoses should be left 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 greater efficiency. So, any means to reduce water consumption might directly lead to a reduction in the quantity of contaminants evacuated through the sewer.

Turnaround and other maintenance activities often result in significant water contamination. To minimise this requires careful planning well in advance, and includes:

- defining 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);
- carefully planning the draining of equipment to avoid undesirable releases to the sewer;
- carefully evaluating the equipment cleaning needs and methods;
- defining a disposal route for all cleaning effluent.

Releases resulting from equipment failure are, by nature, unpredictable. Preventive maintenance for equipment and implementation of a monitoring programme are ways to ensure that these are minimised, for example:

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

Background contamination from foul sewer systems can be minimised by, for example:

- periodically checking sewer inspection chambers for the presence of free hydrocarbons, etc., and vacuum pumping them, if needed, to the slop;
- cleaning of dirty sewers that might cause a significant level of background contamination;
- selected drainage systems (see Section 3.1.5.3.5.2);
- installing a 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 are given in Section 3.3.2.2);
- treatment methods, including:

  ◦ 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 body;
  ◦ final treatment for an individual waste water stream with direct discharge into the receiving water;
  ◦ treatment of 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 slightly contaminated individual waste water streams or non-contaminated rainwater.

The various treatment techniques are described in Section 3.3.

Central treatment may be carried out on site or off site, and potentially together with waste water from other sources (e.g. other industrial installations, municipalities). The connection to a central waste water treatment plant (whether industrial or municipal) can be envisaged only in the case where the sewer and treatment system are capable of transporting and treating the industrial effluent under adequate conditions. In practice, a convention is often established between the operator(s) of the installation(s) generating the effluent and the operator of the central waste water treatment plant (see Section 3.1.3).

3.1.5.3.4.3 Selection of waste gas control system

Description
The selection procedure follows the sequence mentioned in Section 3.1.5.3.4. When planning the modifications entailed by 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 thoroughly assess the effect of any change on the safety of the installation (see Section 3.1.5.3.2).

Source reduction
Controlling emissions requires, firstly, investigation of source reduction opportunities. Careful planning is needed to optimise the pollutant recovery and, consequently, the related investment and operating costs.

Investigation can reveal further opportunities for reduction of emissions at source. 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 of 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.

Treatment technology selection
End-of-pipe 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.

Individual treatment systems are dealt with in Section 3.3.

Achieved environmental benefits
The appropriate selection of a waste gas control system allows for optimising the consumption of materials and energy to achieve the lowest emissions to the environment.

Cross-media effects
None considered of importance.

Operational data
The key design issues for waste gas treatment systems are the flow rate of the gas stream, its temperature, 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 have limitations in this respect, for example:

- only flammable vapours are suitable for incineration;
- contaminants which contain halogens 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, and biofiltration).

The presence of impurities in the off-gas affects the design of the system. Sometimes these impurities have to be removed in a pretreatment step. Impurities that may have to be removed depending on the waste gas control system used include:

- 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 oxidiser or a catalytic filter;
- acids, which affect the biofilter/bioscrubber activity.

The targeted concentration needs to be considered. Most technologies are limited in removal efficiency and condensation, absorption and biofiltration in particular achieve far below 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 as well as the 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 at atmospheric pressure. In order to avoid flashback, i.e. propagation of a flame in the inlet ducts to an incinerator/oxidiser, one has to ensure that the inlet concentration is always well below the LEL. The opposite option – VOC concentration well above the HEL – should 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/oxidiser has to be installed at a location where there is no risk of the presence of flammable vapours, and a detailed analysis is required to ensure the safety of the installation. Also, systems using other technologies should 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 (dedusting of flammable gases should be avoided) and fabric filters (ignition possible because of hot gases, pyrophoric powders and sparks).

Layout constraints may play an important role. Incineration systems have to be located outside 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.

Applicability
Applicable to new and existing installations.

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.

Economics
The investment required for a waste gas treatment system is obviously 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 for ancillary equipment (e.g. a seal drum for an incinerator/oxidiser, 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 catalysts, adsorption media or membranes, costs of chemicals, operations and maintenance, disposal of production residues, pretreatment and post-treatment, etc. When evaluating these, care should be taken to quantify the costs associated with each stage of the operations (normal operation, regeneration, and 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 this temperature requires a fraction of the fuel needed for a simple thermal oxidiser.

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 investment and operating costs.

Driving force for implementation
The driving forces for implementing the technique include ensuring the cost-effectiveness of the choices made and reducing the overall environmental impact of the installation.

Example plants
All plants choose their own waste gas control system.

Reference literature
No reference literature provided.

3.1.5.3.5   Selection of collection system

3.1.5.3.5.1   Overview

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 (see Section 3.1.5.3.5.2) and waste gas ducting (see Section 3.1.5.3.5.3).

3.1.5.3.5.2   Selection of waste water collection and segregation system

Description
Taking into account the results of the waste water inventory/register (see Section 3.1.5.2.3), 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) water treatment facilities;
- separate drains for organic waste water and inorganic waste water without a relevant organic load, which prevents 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.

Segregation of waste water streams is also implemented to:

- pretreat compounds that negatively affect the final waste water treatment plant (e.g. protection of a biological treatment plant against inhibitory or toxic compounds);
- pretreat compounds that are insufficiently abated during final treatment (e.g. toxic compounds, poorly/non-biodegradable organic compounds, organic compounds that are present in high concentrations, or metals during biological treatment);
- pretreat compounds that are otherwise stripped to air from the collection system or during final treatment (e.g. volatile halogenated organic compounds, benzene);
- pretreat compounds that have other negative effects (e.g. corrosion of equipment; unwanted reaction with other substances; contamination of waste water sludge);
- enable material recycling.

Waste water streams that fail to meet the quality requirements for final treatment are subject to special pretreatment operations. Thus, for each waste water stream, the decision process illustrated in Figure 3.3 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 cost-effective. 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).

Achieved environmental benefits
The main benefits of the technique include lowering the volume of waste water requiring treatment, increasing the load of pollutants thus enabling a more efficient treatment as well as allowing material recycling/reuse.

Cross-media effects
None considered of importance.

Operational data
Separate discharge is recommended to avoid a dilution effect of the treated waste water. The more concentrated the effluents that result from separation are, the more generally effective their downstream treatment is.

Applicability
Applicable to new installations. For existing installations, there might be technical and economic difficulties associated with the installation of a waste water separation/segregation system (see Economics below).

Economics
Retrofitting costs associated with the separation/segregation of waste waters can be significant at existing plants. Waste water separation/segregation systems can be installed efficiently at new plants. Savings may be made from the reduction in the water holding capacity needed on the site.

Driving force for implementation
Driving forces for implementing the technique include ensuring the cost-effectiveness of the choices made, enabling material recovery and reducing the overall environmental impact of the installation.

In some countries the mixing of uncontaminated rainwater with other effluents is not permitted.

Example plants
All plants choose their own waste water collection and segregation system.

Reference literature
[148, Degrémont SUEZ 2007]

3.1.5.3.5.3   Selection of waste gas collection systems

Description
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 central treatment system;
- to capture diffuse and/or fugitive emissions (see Section 3.5.4) by extraction hoods and duct them to a treatment unit (less frequently used);
- as flaring systems, which are primarily installed to allow safe disposal of off-gas in emergency situations (see Section 3.5.1.6).

In order to minimise the airflow 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 concerns related to operability (access to equipment), safety (avoiding concentrations too close to the LEL) and hygiene (where operator 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 drops 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 collection 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 include:

- detonation arrestors;
- seal drums;
- 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.

Achieved environmental benefits
The main benefits of the technique include lowering the volume of waste gas to be treated, increasing the concentration of pollutants thus enabling a more efficient treatment as well as allowing material recycling/reuse.

Cross-media effects
The choice of a waste gas collection system may present health and safety concerns that may be under the scope of the ATEX Directives [126, EU 2014] [131, EC 1999].

Operational data
All plants choose their own waste gas collection system.

Applicability
Applicable to new and existing plants.

Economics
No information provided.

Driving force for implementation
Driving forces for implementing the technique include ensuring the cost-effectiveness of the choices made, enabling material recovery and reducing the overall environmental impact of the installation.

Example plants
All plants choose their own waste gas collection system.

Reference literature
[126, EU 2014] [131, EC 1999]

3.1.5.3.6 Implementation of the selected emission control options

Description
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 the 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.

Achieved environmental benefits
A correct implementation of the selected emission control options allows the optimum environmental performance of the systems.

Cross-media effects
None considered important.

Operational data
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. Examples of such measures are given below.

- Organisational measures, e.g. revision of operating procedures or scheduling practices, which can usually be implemented relatively quickly.
- Control measures, e.g. computer control optimisation routines, which 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, which 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.

Applicability
Applicable to new and existing installations.

Economics
Cost savings are expected from a correct implementation of the emission control systems due to reducing or avoiding maintenance operations.

Driving force for implementation
Reducing the environmental impact and reducing maintenance costs are the main driving forces for implementation.

Example plants
All plants make an appropriate choice of their waste gas treatment considering a number of factors.

Reference literature
No reference literature provided.

3.1.5.3.7   Quality control methods

Description
Quality control methods are tools which are used as a 'troubleshooter' 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 [64, Hartung 1993]:

- 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. These methods are illustrated under Operational data below for waste water treatment, with the control method for waste gas treatment being similar.

Achieved environmental benefits
Quality control measures enable a timely detection and implementation of corrective measures to ensure the optimum functioning of the pollution treatment systems.

Cross-media effects
None considered important.

Operational data
Exerting control [64, Hartung 1993]
Some variables can be controlled by the operator of a WWTP, such as clarifier blowdown, dissolved oxygen and chemical feed, which can be adjusted when circumstances dictate. Other variables are beyond the control of the operator of the WWTP, 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. Also, good communication between the operator of the installation producing waste water and the operator of the WWTP is essential to ensure the best possible quality of the effluent discharged to the receiving water. Conventions are tools that can help in this respect (see Section 3.1.3).

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. Online testing and monitoring will give the WWTP advance warning of step changes that occur to its input.

Control/improvement [64, Hartung 1993]
The common mode of operating a WWTP is that of process control. Only those operations that need to be carried out to meet standards and stay within control regarding effluent quality are performed, thus losing part of the 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.

Quality improvement tools [64, Hartung 1993]

The goal of quality improvement is to reject the typical standards and reach a level of performance never before achieved, 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 and effect diagram** in the form of an Ishikawa Fishbone diagram, as shown in Figure 3.4, provides an effective way to organise and display various ideas about what the root causes might be.
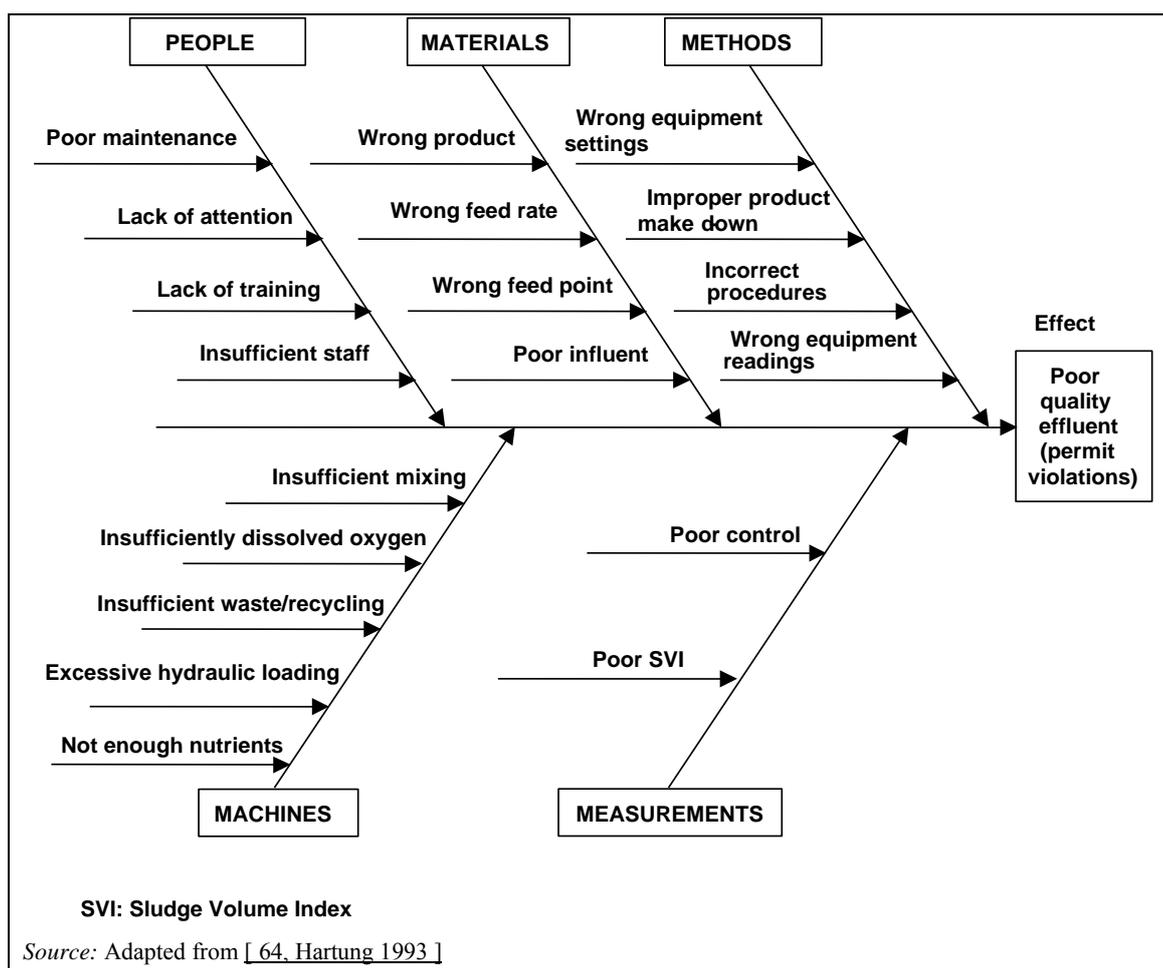
Figure 3.4: **Cause and effect diagram (Ishikawa Fishbone diagram) for problem solving and quality improvement of poor quality effluent**

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 few vital 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 to 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 an identification of special problems.

The third step on the way to improving 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 non-conformance 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?

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 within 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 the control range or permit limits.

When the statistical limits defined by the process fall outside the operating standards or requirements, the operator is probably reacting properly to changes noticed in the process. The operator is wrestling with a system that is expected to operate within a range, within which it is statistically not possible to operate 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.

Applicability
Applicable to new and existing plants.

Economics
No information provided.

Driving force for implementation
Quality control methods are implemented as part of the environmental management system.

Example plants
No information provided.

Reference literature
[64, Hartung 1993]

3.1.5.4   Strategic management tools

3.1.5.4.1   Overview

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 other chemical BREFs or the REF document on Economic and Cross-media Effects (ECM) [112, COM 2006]. Examples of such tools that evaluate environmental and economic options are:

- risk assessment;
- benchmarking.

3.1.5.4.2   Risk assessment

Description
Risk assessment is a common methodology to calculate human and ecological risks as a result of the activities of production processes. It may take into account continuous and discontinuous emissions, leakage losses, and accidental emissions for example. It is a stepwise and iterative process, comprised of at least the first of five steps [67, Ullmann's 2000]:

- 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 [67, Ullmann's 2000]. 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 for example that:

- 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 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-making 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 political process [67, Ullmann's 2000], which normally includes risk-benefit considerations including

cost allocation, and often entails subjective judgement. These thoughts are taken into account in the REF document on Economics and Cross-media Effects (ECM) [112, COM 2006].

Computer programs exist for the application of risk assessment processes [24, InfoMil 2000].

Achieved environmental benefits
Risk assessment tools help plant management to reduce the risk and to mitigate the consequences of adverse events.

Cross-media effects
None considered important.

Operational data
No information provided.

Applicability
Applicable to new and existing installations.

Economics
No information provided.

Driving force for implementation
Driving forces for implementation include the safety of the workers and the protection of the production facility from adverse events.

Example plants
No information provided.

Reference literature
[24, InfoMil 2000] [67, Ullmann's 2000], [112, COM 2006]

3.1.5.4.3 Benchmarking

Description
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 their own way of performing, e.g. their 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.

Achieved environmental benefits
Benchmarking can lead to improvements that are beneficial with respect to the overall environmental performance of the installation.

Cross-media effects
There are no cross-media effects associated with benchmarking.

Operational data
No information provided.

Applicability
Applicable to new and existing installations.

Economics
The collection and analysis of data needed for a benchmarking exercise imply some costs. These may vary greatly depending on the industrial sector or subsector considered for the benchmark exercise.

Driving force for implementation
The main driving force for implementation is to optimise plant operation, including its environmental performance.

Example plants
No information provided.

Reference literature
No reference literature provided.

3.1.5.5 Safety and emergency tools

3.1.5.5.1 Overview

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. Specific laws (especially the Seveso III Directive [145, EU 2012]) exist to prevent major accident hazards involving dangerous substances from occurring in the first place and, should they occur, to limit their consequences.

Spillages of chemicals and oil are obvious threats on chemical sites. However, materials which are not hazardous to humans may also cause serious environmental problems, as can the run-off water 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 [74, Environmental Alliance (UK) 2000].

Pollutants may escape from the site into the water environment by a number of pathways, such as [74, Environmental Alliance (UK) 2000]:

- 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 a potential risk to groundwater;
- via the foul drainage system, with pollutants either passing unaltered through a sewerage treatment works or affecting the performance of the works, resulting in further environmental damage;
- through atmospheric deposition, such as vapour plumes.

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 that can be mixed with water such as acids or ammonia, which can be dowsed by a water curtain and thus become an item for waste water treatment.

3.1.5.5.2   Managing firefighting water and major spillages

Description
The main focus of firefighting 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 3.1.5.5.3) to reduce the impact of any unplanned event that does occur [74, Environmental Alliance (UK) 2000].

The first step, however, is to consider the firefighting strategies and possible methods to reduce the amount of firefighting water run-off generated, e.g. by the use of sprays rather than jets, controlled burn and the possible recycling of firefighting water, where safe and practicable [74, Environmental Alliance (UK) 2000].

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 is helpful (see Section 3.1.5.4.2). The operator should consider the hazardous materials on site, the risks posed by accidents, fire, flooding and vandalism, the 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 firefighting 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 [74, Environmental Alliance (UK) 2000].

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

- the potential harm that could be caused by the contaminated firefighting water (evaluation methods based on risk phrases – as defined in Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures [66, Regulation EC/1272/2008 2008] – can be used as well as systems like the German VCI concept on firefighting 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;
- firefighting and cooling water;
- foam (as a firefighting medium);
- dynamic effects, such as initial surge of liquid or windblown 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, and the lagoons 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 of or the whole site;
- oil separators (see Section 3.3.2.3.3.8).

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, firefighting 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 [74, Environmental Alliance (UK) 2000].

Examples of emergency containment measures include [74, Environmental Alliance (UK) 2000]:

- 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 3.1.5.5.3) should identify pollution prevention equipment and materials and their location. Such materials and equipment are [74, Environmental Alliance (UK) 2000]:

- 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 firefighting water. Where reuse is possible, the spilled material should be returned to storage on site. If off-site disposal is required, it can be done by means of [74, Environmental Alliance (UK) 2000]:

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

Treatment/disposal has to take into account persistent and/or toxic contaminants that may also originate from firefighting foam materials (e.g. aqueous film-forming foams containing perfluorinated chemicals [82, Seow 2013]). As a precautionary measure, firefighting materials should be assessed to select the most suitable option with the least impact on the environment.

Achieved environmental benefits
The environmental benefit of the technique is to minimise the environmental impact of firefighting water and spillages.

Cross-media effects
None considered important.

Operational data
No information provided.

Applicability
Applicable to new and existing plants.

Economics
No information provided.

Driving force for implementation
Managing firefighting water and spillages is required to reduce the environmental impact of incidents/accidents.

Example plants
Seveso sites (high threshold) are example installations.

Reference literature
[66, Regulation EC/1272/2008 2008] [74, Environmental Alliance (UK) 2000] [82, Seow 2013]

3.1.5.5.3 Pollution incident response planning

Description
A pollution incident response plan, as mentioned several times in Section 3.1.5.5.2, is mainly a strategy to spread all information needed in the most efficient way to all those whom it may concern. The general way to implement such a plan is by [75, Environmental Alliance (UK) 2000]:

- 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 sewer operators, EHS executives, keyholders and contact staff, specialist advisers, etc.;
- 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 an 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 Section 7.4, Annex IV.

Emergency planning and response is often an issue which needs to be coordinated at the site level. Sharing resources (e.g. containment systems, emergency materials and equipment, firefighter teams) and defining shared emergency procedures have important advantages. Conventions established between operators of a site (see Section 3.1.3) are a way to clarify roles and responsibilities in this matter.

Achieved environmental benefits
Mitigating the effects on the environment of incidents/accidents.

Cross-media effects
There are no cross-media effects associated with this technique.

Operational data
No information provided.

Applicability
Applicable to all plants.

Economics
No information provided.

Driving force for implementation
The technique is required by legislation for the plants which have a high potential for pollution.

Reference literature
[75, Environmental Alliance (UK) 2000]

3.2 Monitoring

3.2.1 Overview

Monitoring forms a bridge between the inventory/register and operational tools (see Sections 3.1.5.2 and 3.1.5.3), but is also connected with strategic and safety tools (see Sections 3.1.5.4 and 3.1.5.5). The bulk of the information provided by inventory tools, e.g. the stream inventory/register (see Section 3.1.5.2.3), 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 environmental targets set are met and to identify and help to track accidents (incidents).

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 [252, Ullmann's 2012]:

- 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 3.2.2.3);
- 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 Reference Report on Monitoring of Emissions to Air and Water from IED installations (ROM) exists to which the reader is referred for further information [101, COM 2016]. Monitoring in the context of waste water and waste gas is further dealt with in Section 3.3.

3.2.2   Monitoring of emissions to water

3.2.2.1   Monitoring of influent and effluent waste waters of a WWTP

Description
Proper operation of a WWTP requires the monitoring and targeted adjustment of various process parameters in the influent and effluent of the WWTP. Monitoring of the relevant parameters can be accomplished by online measurements (that facilitate rapid intervention and control) or analytical results derived from waste water samples [251, Ullmann's 2000]. Parameters to be monitored and the frequency of monitoring depend on the characteristics of the waste water to be treated, the final effluent discharge medium and the waste water treatment techniques used within the WWTP.

Important parameters are also monitored at the level of each waste water treatment technique comprising the WWTP to ensure the proper operation of the techniques and the subsequent treatment steps. This specific monitoring is not described in this section but is generally addressed, if relevant, in the sections dealing with individual treatment techniques (see Section 3.3.2.3).

Table 3.3 summarises the information collected from the questionnaires on parameters monitored in the influent and effluent of the WWTPs. The data collection was restricted to a set of common parameters and did not include, for example, the common chromatographic detection of site-specific organic compounds. When data on influent or effluent concentrations were provided, these data were usually accompanied with some information on the monitoring. For example, TSS values in the effluent were reported by 76 out of 95 directly discharging WWTPs, and for 65 (or 86 %) of these some information on the monitoring was provided. However, this information was often incomplete (e.g. on frequency, sampling regime, or analytical method used).

The parameters monitored have been grouped into two categories: routinely monitored parameters and non-routinely monitored parameters. Routinely monitored parameters are the ones for which data were reported in more than 50 % of the 95 questionnaires analysed. Non-routinely monitored parameters are the ones for which data were reported in less than 50 % of the 95 questionnaires analysed. The monitoring frequencies of the parameters have also been extracted from the questionnaires as provided in Table 3.3. However, the measurement frequency was not reported in all questionnaires. The monitoring frequency of any parameter depends on many factors such as the origin of the waste water and type of contamination (e.g. if the influent waste water contains high AOX levels, then the frequency of AOX measurements might be higher), the influent load of contaminants (e.g. high concentrations of heavy metals), type of recipient water body (whether it is a creek or a sea will affect the frequency of monitoring of a certain parameter), the effluent waste water flow rate compared to the flow rate of the water body and the monitoring requirements set by the Member States (see also the Reference Report on Monitoring of Emissions to Air and Water from IED installations (ROM) [101, COM 2016]).

Regarding the monitoring of emissions, they shall be carried out in accordance with EN standards or, if EN standards are not available, ISO, national or other international standards which ensure the provision of data of an equivalent scientific quality.

Table 3.3:   Monitoring regimes reported for the WWTPs

<table>
<tr><th></th><th>Parameter</th><th>Frequency</th></tr>
<tr><td rowspan="22">Influent to the WWTP</td><td colspan="2" align="center">Routinely monitored</td></tr>
<tr><td>Waste water flow</td><td>Continuous</td></tr>
<tr><td>pH</td><td>Continuous</td></tr>
<tr><td>Temperature</td><td>Continuous</td></tr>
<tr><td>COD</td><td>Continuous
Daily/weekly/monthly</td></tr>
<tr><td colspan="2" align="center">Non-routinely monitored</td></tr>
<tr><td>TOC</td><td>Continuous
Daily/weekly/monthly</td></tr>
<tr><td>BOD_5</td><td>Daily/weekly/monthly</td></tr>
<tr><td>Total suspended solids (TSS)</td><td>Daily or other</td></tr>
<tr><td>Total nitrogen (TN) [1]</td><td>Continuous
Daily/weekly/monthly</td></tr>
<tr><td>Total inorganic nitrogen (N_{inorg}) [1]</td><td>Daily/weekly or other</td></tr>
<tr><td>Ammonia (NH_4-N)</td><td>Daily/weekly or other</td></tr>
<tr><td>Nitrite (NO_2-N)</td><td>Daily/weekly or other</td></tr>
<tr><td>Nitrate (NO_3-N)</td><td>Daily/weekly or other</td></tr>
<tr><td>Total phosphorus (TP)</td><td>Continuous
Daily/weekly/monthly or other</td></tr>
<tr><td>Orthophosphate (PO_4-P) [2]</td><td>Daily/weekly</td></tr>
<tr><td>AOX</td><td>Daily/weekly/monthly</td></tr>
<tr><td>Heavy metals [3]</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td>Bacteria toxicity [2]</td><td>Daily/monthly</td></tr>
<tr><td>Phenols [2]</td><td>Daily/weekly or other</td></tr>
<tr><td>Chloride [2]</td><td>Daily/weekly or other</td></tr>
<tr><td>Sulphate [2]</td><td>Daily/weekly/monthly</td></tr>
<tr><td>Cyanide(free) [2]</td><td>No information provided</td></tr>
<tr><td>Other [4]</td><td>Site-specific</td></tr>
<tr><td rowspan="24">Effluent from the WWTP</td><td colspan="2" align="center">Routinely monitored</td></tr>
<tr><td>Waste water flow</td><td>Continuous</td></tr>
<tr><td>pH</td><td>Continuous
Daily or other</td></tr>
<tr><td>Temperature</td><td>Continuous</td></tr>
<tr><td>COD</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td>BOD_5</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td>Total suspended solids (TSS)</td><td>Continuous
Daily/weekly/monthly or other</td></tr>
<tr><td>Total nitrogen (TN) [1]</td><td>Daily/weekly or other</td></tr>
<tr><td>Total inorganic nitrogen (N_{inorg}) [1]</td><td>Daily/weekly or other</td></tr>
<tr><td>Ammonia (NH_4-N)</td><td>Daily/weekly or other</td></tr>
<tr><td>Nitrite (NO_2-N)</td><td>Daily/weekly or other</td></tr>
<tr><td>Nitrate (NO_3-N)</td><td>Daily/weekly or other</td></tr>
<tr><td>Total phosphorus (TP)</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td>Orthophosphate (PO_4-P) [2]</td><td>Daily/weekly</td></tr>
<tr><td>Heavy metals [3]</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td>Chloride [2]</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td colspan="2" align="center">Non-routinely monitored</td></tr>
<tr><td>TOC</td><td>Daily or other</td></tr>
<tr><td>AOX [2]</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td>Toxicity (e.g. fish or fish egg, daphnia, algae, luminescence) [2]</td><td>Monthly or other</td></tr>
<tr><td>Sulphate [2]</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td>Phenols [2]</td><td>Daily/weekly/monthly or other</td></tr>
<tr><td>Cyanide (free) [2]</td><td>Monthly or other</td></tr>
<tr><td>Other (hydrocarbons, fluoride, etc.) [4]</td><td>Site-specific</td></tr>
</table>

[1] Refers only to biological WWTPs.
[2] Corresponding data were only collected during the first survey.
[3] The following heavy metals were asked for in both surveys: Cd, Cr, Cu, Hg, Ni, Pb, Zn. The heavy metals monitored are site-specific based on the characteristics of the waste water to be treated and the final effluent discharge medium.
[4] Other parameters (e.g. hydrocarbons, fluoride) can be included in the monitoring regime depending on the characteristics of the waste water to be treated, the type of treatment techniques used and the final effluent discharge medium.

Source: [222, CWW TWG 2013].

Achieved environmental benefits
Monitoring of influent and effluent waste water of a WWTP helps to maintain the proper operation of the WWTP and to detect accidental releases and thus helps to prevent any possible adverse environmental effects upon discharge of waste waters.

Cross-media effects
Some equipment, chemicals and energy are required for carrying out monitoring. The COD measurement relies on the use of very toxic compounds (i.e. mercury and chromate).

Operational data
The parameters to be monitored in the influent to, and effluent from, the WWTP and the frequencies of monitoring depend on the characteristics of the waste water, the final effluent discharge medium and the type of treatment techniques used.

Table 3.4 gives the monitoring regime of a WWTP from Germany (WWTP #06).

Table 3.4:   Monitoring regime of an example WWTP

Parameter	Influent	Effluent
Waste water flow	Continuous	Continuous
pH	Continuous	Continuous
Temperature	Continuous	Continuous
TOC	Monthly mixed sample	24-h mixed sample, daily
BOD$_5$	24-h mixed sample, weekly	24-h mixed sample, weekly
COD	Monthly mixed sample	Monthly mixed sample
TSS	NM	Continuous, as turbidity
AOX	Monthly mixed sample	24-h mixed sample, weekly + monthly mixed sample
Total chromium	Monthly mixed sample	Monthly mixed sample
Total copper	Monthly mixed sample	24-h mixed sample, weekly + monthly mixed sample
TN (as N)	Monthly mixed sample	Total inorganic N
Ammonia (NH$_4$-N)	NM	24-h mixed sample, daily
Nitrite (NO$_2$-N)	NM	24-h mixed sample, daily
Nitrate (NO$_3$-N)	NM	24-h mixed sample, daily
TP	Monthly mixed sample	24-h mixed sample, weekly + monthly mixed sample
Chloride	NM	24-h mixed sample, daily
Sulphate	NM	24-h mixed sample, daily + monthly mixed sample
NB: NM = not monitored.		
Source: [222, CWW TWG 2013].		

The monitoring regime given in Table 3.4 is specific to the WWTP in question and cannot be generalised to other WWTPs.

Applicability
Generally applicable to all WWTPs.

Economics
The costs associated with monitoring of influent and effluent waste water of a WWTP relate to personnel and equipment used for sampling and measurement.

Driving force for implementation
To ensure the proper operation of the WWTP and to ensure that the required quality of the effluent waste water from the WWTP is met and in line with the effluent discharge criteria are the driving forces for the implementation of this technique.

Example plants
All WWTPs have a specific monitoring regime depending on the raw waste water characteristics, treatment techniques used and the final effluent discharge medium [222, CWW TWG 2013].

Reference literature
[101, COM 2016] [222, CWW TWG 2013] [251, Ullmann's 2000]

3.2.2.2 Toxicity tests

Description
Toxicity tests consist in exposing test organisms to an environment (here an original or diluted waste water sample) to determine the effects on physiological properties, survival, growth or reproduction. Different organisms representing distinct trophic levels are used including algae, bacteria, plants, invertebrates, fish and fish eggs. Toxicity tests are carried out in laboratories (also called laboratory bioassays) where test organisms (mainly from standardised cultures) are exposed to waste water that has been transferred to the laboratory.

Table 3.5 presents examples of available standard methods that can be used to conduct toxicity tests.

Table 3.5: **Example of standard methods that can be used to conduct toxicity tests**

Test organisms	Standards
Algae	**EN ISO 8692:2012**; Water quality – Freshwater algal growth inhibition test with unicellular green algae
	EN ISO 10253:2006; Water quality – Marine algal growth inhibition test with *Skeletonema costatum* and *Phaeodactylum tricornutum*
	EN ISO 10710:2013; Water quality – Growth inhibition test with the marine and brackish water macroalga *Ceramium tenuicorne*
Bacteria	**EN ISO 11348–1 to –3:2008**; Water quality – Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri* (Luminescent bacteria test) – Part 1: Method using freshly prepared bacteria, Part 2: Method using liquid-dried bacteria, Part 3: Method using freeze-dried bacteria **EN ISO 10712:1995**; Water quality – *Pseudomonas putida* growth inhibition test (*Pseudomonas* cell multiplication inhibition test)
	ISO 11350:2012; Water quality – Determination of the genotoxicity of water and waste water – *Salmonella/microsome* fluctuation test (Ames fluctuation test)
	ISO 15522:1999; Water quality – Determination of the inhibitory effect of water constituents on the growth of activated sludge microorganisms
	ISO 13829:2000; Water quality – Determination of the genotoxicity of water and waste water using the umu-test
Plants	**EN ISO 20079:2006**; Water quality – Determination of the toxic effect of water constituents and waste water on duckweed (*Lemna minor*) – Duckweed growth inhibition test
Rotifers	**ISO 20666:2008**; Water quality – Determination of the chronic toxicity to *Brachionus calyciflorus* in 48 hours
Crustaceans	**EN ISO 6341:2012**; Water quality – Determination of the inhibition of the mobility of Daphnia magna Straus (*Cladocera, Crustacea*) – Acute toxicity test
	ISO 10706:2000; Water quality – Determination of long term toxicity of substances to Daphnia magna Straus (*Cladocera, Crustacea*)
	ISO 20665:2008; Water quality – Determination of the chronic toxicity to Ceriodaphnia dubia
	ISO 14669:1999; Water quality – Determination of acute lethal toxicity to marine copepods (Copepoda, Crustacea)
Fish and fish eggs	**EN ISO 7346–1:1997**; Water quality – Determination of the acute lethal toxicity of substances to a freshwater fish Brachydanio rerio Hamilton-Buchanan (*Teleostei, Cyprinidae*) – Part 1: Static method, Part 2: Semi-static method, Part 3: Flow-through method
	EN ISO 15088:2008; Water quality – Determination of the acute toxicity of waste water to zebrafish eggs (Danio rerio)

In stream bioassays, living organisms (e.g. fish) are placed into the water stream to be studied (e.g. in cages upstream and downstream of effluent discharges). Stream bioassays are at an experimental stage.

The use of toxicity tests is less comprehensive than whole effluent assessment (WEA, see Section 3.2.2.3) which also includes persistence and bioaccumulation.

Achieved environmental benefits
Toxicity tests allow for an integrated assessment of the properties of a waste water sample (including synergistic/antagonistic effects) that cannot be achieved by analysing single substances or other chemical sum parameters. They provide the basis for measures to control pollution and to minimise the ecotoxic impact of waste water effluents.

Cross-media effects
Some equipment, chemicals and energy are required for carrying out toxicity tests. Some toxicity tests affect animal welfare (e.g. toxicity tests using fish).

Operational data

There is a lot of experience with toxicity measurements and two different procedures are usually applied for the evaluation of toxicity data:

- **Response concentration**. The EC_X/LC_X (effect/lethal concentration) approach using statistical data analysis where at least five data pairs of concentration/response between 0 % and 100 % response are needed. Typical results are EC_{50}, EC_{20} or EC_{10}, the concentration that has a particular effect on 50 %, 20 % or 10 % of the population. The EC_X/LC_X methodology is usually applied to single substances. However, dilution values for a water sample representing a given response level can in principle also be obtained from the LID approach (see below) as described in ISO TS 20281 [100, ISO 2006].
- **Threshold concentration**. The concentration having no statistically significant adverse effect is the no observed adverse effect concentration (NOAEC). In the case of waste water, the concentration of the substance(s) is generally not known. The LID (Lowest Ineffective Dilution) approach therefore uses dilutions of the original waste water with defined ratios of sample and dilution water until no effects are observed. A statistical evaluation of the concentration/response relationship is not necessary, because a yes/no-type decision is made with regard to the defined effect level described in the respective standard (usually 10 % or 20 % effect in comparison to test control). This makes the test design concerning the test concentrations easier. Statistical requirements for the calculation of EC values are often not met for moderately toxic samples. LID values are used for monitoring the total waste water effluents of many German chemical sites [105, COM 2006].

Toxicity data may also be expressed as toxic units (TU), an acute toxic unit TU_a being $100/EC_{50}$, and a chronic toxic unit TU_c being $100/NOAEC$ or $100/EC_{10}$.

Chronic toxicity tests are less widespread than acute toxicity tests and short-term chronic tests are to be preferred in order to avoid any possible change in the characteristics of the effluent during the test [146, TOTAL 2009].

Toxicity tests are generally used in at least five EU Member States for setting emission limit values (ELVs) [139, COHIBA 2010]:

- Germany: Five different toxicity tests are used in combination for all chemical sites (fish egg, daphnia, algae, luminescent bacteria, genotoxicity). These tests have been in use since 1999. Toxicity tests with fish were already used since the late 1980s [65, OSPAR 2000] [105, COM 2006] [135, LANUV NRW 2009].
- Ireland has mandatory ELVs in terms of toxicity units for direct discharges from IED plants. Toxicity tests may also be required for indirect discharges.
- Austria has mandatory ELVs for toxicity for several subsectors of the chemical industry. Up to four toxicity tests are used in combination (fish, daphnia, algae, and luminescent bacteria).
- Lithuania requires effluents entering surface waters to pass acute daphnia tests.
- Italy has obligatory acute toxicity tests (e.g. with daphnia, algae or luminescent bacteria). The legal consequences of exceeding an emission limit value are, however, less stringent than for other parameters.

Furthermore, other EU Member States sometimes use toxicity tests in permits: Flanders (Belgium), Denmark, Finland and Sweden.

In the course of the last twenty years, biomonitoring in Germany resulted in thousands of biotest data from the chemical industry. Recent results can be found in [135, LANUV NRW 2009]. Earlier statistics can be found in the LVOC BREF [104, COM 2003].

Experience of some years shows that [105, COM 2006]:

- generally, the data derived from using different test species (algae, daphnia, bacteria, fish eggs) complement each other;
- even at a larger complex production site, it is usually technically possible to identify the cause of residual acute toxicity and to minimise the effects;
- the sampling frequency should correspond to the frequency of changes in the production spectrum (in the given example [105, COM 2006], 20 samples were tested per year).

Applicability
Toxicity tests are especially applicable where other parameters indicate variations in the performance of the biological WWTP or where toxicity is already identified as a major concern due to the production spectrum (e.g. biologically active ingredients).

This technique is generally applicable to identify situations where a production site has an inherent toxicity problem which is not easily identified by the observation of other parameters.

The monitoring frequency for toxicity tests may be based on a risk assessment, after an initial characterisation.

Toxicity tests are rarely carried out online. The time needed to obtain the results, typically between 24 hours and 96 hours, does not allow the waste water treatment to be directly controlled.

Economics
Economic factors include:

- costs for sampling and measurements;
- high value of the obtained information.

Driving force for implementation
Reducing the residual acute toxicity in effluents is the driving force for implementing the technique.

Example plants
Toxicity tests of waste water effluents are used at chemical sites in a number of EU Member States.

Reference literature
[65, OSPAR 2000] [100, ISO 2006] [104, COM 2003] [105, COM 2006] [135, LANUV NRW 2009] [139, COHIBA 2010] [146, TOTAL 2009]

3.2.2.3 Whole effluent assessment (WEA)

Description
Chemicals which are persistent, liable to bioaccumulation and/or toxic (PBT) are of specific concern to the aquatic environment. WEA aims at estimating the persistency, bioaccumulation potential and toxicity of waste water as a whole. In contrast to this, the substance-orientated approach focuses on measuring hazardous substances that have been selected and prioritised using the PBT criteria.

The aim of WEA is to assess the possibly hazardous character of effluents, which would be insufficiently controlled when relying only on the physical and chemical indications provided by the conventional environmental variables (e.g. TOC, COD) or by limits set on individual chemicals.

The advantages of using WEA are as follows:

- All waste water compounds are considered regardless of their origin. The compounds do not necessarily need to be identified. Side products and metabolites are assessed as well.
- Toxic effects on aquatic organisms are directly displayed; combined/synergistic effects of several compounds are also considered.
- The sources of hazardous effluents (production steps or hot spots) inside industrial areas can often be identified (backtracking).

Generally, WEA can be used as a tool within an EMS (see Section 3.1.2). WEA can be one of the measures used in an effluent stream inventory/register as described in Section 3.1.5.2.3.

Achieved environmental benefits
WEA allows for a way to monitor complex and variable waste water effluents including the possible synergistic effects of chemicals.

Cross-media effects
Some equipment, chemicals and energy are required for carrying out WEA. Some toxicity tests affect animal welfare (e.g. toxicity tests using fish).

Operational data
Test methods and test sequences
The methodology of WEA is aimed at determining possible adverse effects of effluents and addresses basically the same effect measurements (PBT) that are used in a substance-orientated approach.

Persistence is typically studied in 28-day biological degradability tests, and gives information on whether the biotreatment already given is adequate or whether such treatment should be considered for untreated waste water. It is often quantified by measurements of dissolved organic carbon (DOC), but CO_2 evolution is an alternative and there are others (see ISO/TR 15462:1997 Water quality – Selection of tests for biodegradability). Furthermore, if followed by toxicity tests, an indication of the potential for the reduction of toxicity is given.

Liability to bioaccumulate is often measured (both before and after biodegradation) by chemical analysis showing a partition of an extract of the sample between water and a less polar phase (liquid/liquid extraction (LLE)), alternatively directly extracting the sample with a solid phase polymer (solid-phase microextraction (SPME)). Quantification is done by gas or liquid chromatography.

Toxicity tests are described in Section 3.2.2.2. The advantage of using toxicity tests over chemical analyses of single substances is that the hazardous properties of the water samples are determined in an integrated manner and interactive/synergistic effects which may occur in the presence of several pollutants are directly accounted for. In some cases, toxicity tests could be quicker and cheaper than extensive chemical characterisation associated with ecotoxicological characteristics and thereby simplify regulation.

The application of WEA presents challenges for the scientific community. They include the following:

- A dominating focus on the toxicity component of PBT in combination with a lack of agreement on standardised tests for bioaccumulation and persistence.
- The protection of sediments is taken into account in WEA thanks to the PB substances that are likely to adsorb on sediments; the food chain exposure is taken into account in the bioaccumulation tests. Some methods are under standardisation in ISO to assess adverse effects on soil (e.g. determination of fresh water sediment chronic toxicity to *Heterocypris incongruens*; determination of the toxic effect of sediment and soil samples

on growth, fertility and reproduction of *Caenorhabditis elegans*; determination of the toxic effect of sediment and soil on the growth behaviour of *Myriophyllum aquaticum*).

- Finding laboratories that are competent to routinely run WEA tests. The availability of the laboratory is an issue because the effluent samples refrigerated for 24 hours must be tested as soon as they arrive at the laboratory; the effect of freezing on effluent bioaccumulation, persistence and on acute and chronic toxicity cannot be disregarded [146, TOTAL 2009]. Good planning and coordination between the operator of the installation and the laboratory is key to the successful application of WEA tests.

It is therefore important to communicate the results of WEA testing with an adequate account of the effluent sampling, applied test methods, and the statistical analyses applied to the data. Further agreement on such issues has been reached in the last decade, however work is still required in particular concerning bioaccumulation and degradability methods.

Applicability
Below, the reader will find the potential applications of WEA divided into sections with a brief description of each.

Regulations or guidance on effluent ecotoxicity
Some jurisdictions set numerical ecotoxicity criteria in discharge permits, while others use ecotoxicity data as a planning and assessment tool (see Section 3.2.2.2). Establishing ecotoxicity criteria ensures consistent evaluation of effluents: enforcement or management action is usually taken only when the effluent repeatedly fails the ecotoxicity criteria. Alternatively, less formal approaches to using ecotoxicity data can reduce uncertainties about the risks of effluent discharge by complementing conventional chemical effluent data. In addition to ecotoxicity data, evaluations of persistence and bioaccumulation can be used in the same way [35, De Maagd 2000].

Ranking the environmental risk of discharges to an aquatic system
WEA can be used to evaluate relative risks posed by multiple discharges 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. TRE can be defined as site-specific studies conducted in a step-wise procedure designed to [27, US EPA 1991]:

- identify the substance 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 substance responsible for effluent toxicity (they 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. 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 water treatment measures
Identification/reduction evaluations (as described above) can be used to predict the effectiveness of various waste water 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 water 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 the treatment over time.

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 is caused by an effluent discharge could be tested using carefully designed WEA. In addition, methods for effluent assessment can be used to evaluate the receiving environment quality, allowing a direct comparison between the effluent and the recipient water. This is recommended procedure in some countries.

Site-specific hazard/risk assessment
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 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 still developing and is mostly focused on toxicity tests (see Section 3.2.2.2).

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 online 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.

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 the ecotoxicological evaluation 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 Environment Agency drafted a background document on the use of WEA in waste water evaluation [65, OSPAR 2000]. Subsequently, an intersessional expert group (IEG) worked for several years developing WEA within the context of OSPAR's Hazardous Substances Strategy [129, OSPAR 2007].

Availability of laboratories to conduct tests in WEA may be a limitation to the use of the technique.

Economics
For a complex effluent, WEA is expected to be less expensive than comprehensive chemical and ecotoxicological analyses on the substances present in the effluent.

Substance by substance analysis will often be preferred for processes with few substances, or where there is no chemical reaction involved (typically blending, such as paint manufacture), whereas WEA is normally the first choice for chemical processes. It may well be augmented by analysis of specific known substances, especially hazardous ones. Indications on how to use WEA in a cost-effective manner can be found in [130, OSPAR 2007].

Driving force for implementation
WEA provides an additional and more direct means of assessing the potential impact of effluents on the aquatic environment and is playing an increasing role in the regulation of discharges, supplementing or sometimes replacing the common measurements of effluent quality in environmental monitoring and risk assessment. In Germany, toxicity tests are routinely used (i.e. LID approach, see above as well Section 3.2.2.2) for monitoring total water effluents [135, LANUV NRW 2009] [105, COM 2006].

With WEA test methods, an indication of the environmental significance of a complex effluent can be determined. This is usually quicker and cheaper than extensive chemical characterisation and thereby simplifies regulation.

Example plants
- Chemical manufacturing site of pharmaceutical ingredients, Germany [132,CEFIC 2009] and several other chemical installations (e.g. OFC plants) in Germany [135, LANUV NRW 2009] [105, COM 2006].
- Chemical installation producing intermediates for the pharmaceutical industry in the Netherlands [133, ECETOC 2004].
- Conglomerate of many petrochemical and raw material-producing plants in the Netherlands [133, ECETOC 2004].

Reference literature
[27, US EPA 1991] [35, De Maagd 2000] [65, OSPAR 2000] [105, COM 2006] [128, Unden 2009] [129, OSPAR 2007] [130, OSPAR 2007] [132, CEFIC 2009] [133, ECETOC 2004] [135, LANUV NRW 2009] [146, TOTAL 2009]

3.2.3   Monitoring of emissions to air

3.2.3.1   Waste gas emission quantification

Description
The waste gas emissions from some sources may have different causes, and therefore the emissions 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
To prepare a waste gas inventory/register, 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 emission. In particular, uncaptured (or diffuse) emissions are very difficult to measure (see Section 3.5.4). They require quantification by contributing cause.

The examples below are offered by way of illustration.

- The emission from a product (normally VOCs) 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 (see the OFC BREF for an example [105, COM 2006]).

- 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 airflow rate and waste gas concentration (preferably at different stages of the process). This measurement can, however, be relatively expensive 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 often varies over 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 the 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 flue-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 (however, because abatement efficiencies may vary, regular checks by measurements might be needed).

- Uncaptured emissions are, by nature, difficult and often expensive to measure and frequently 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 made.

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.

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 have to be made in sufficient number to account for the full range of variability. A yearly material balance needs to take the actual yearly production into account to properly reflect the grade effect.

Examples of quantification of emissions are given below:

- Storage tank emission calculations can be based on the methodology developed by the United States Environmental Protection Agency (US EPA) [29, US EPA 1995]. 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 aboveground atmospheric tanks. However, breathing losses from underground tanks or tanks with a pressure set 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 is 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 to the other emissions. If detailed calculations are required, the 'AP 42 Compilation of Air Pollutant Emission Factors' or the TANKS computer tool [30, US EPA 1999] developed by the US EPA, which is a computerised version of the US EPA calculation method, can be used. Further techniques to calculate emissions from storage tanks are described in the EFS BREF [113, COM 2006].

- Emissions from handling can be calculated assuming a vapour content of the air exhausted from the container which is loaded depending on 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 [13, CEFIC 1999]:
  ◦ 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 US EPA 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). An additional description is provided in the US EPA-453 Protocol [79, US EPA 1995], which is also detailed within the IMPEL project entitled 'Diffuse VOC Emissions' [81, IMPEL 2000]. 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. For small plants or plants handling low amounts of VOCs, such calculations can be used to provide a first indication of the order of magnitude of the fugitive emission. If these calculations show that emissions are indeed low and the benefit of LDAR would be small, no further action is required. If the equipment leak emissions become significant, a monitoring and maintenance programme (also called leak detection and repair or LDAR (see Section 3.5.4.4)) should be implemented, entailing the measurement of each potential leak point and the opportunity for repair of any leaks discovered. This work requires skill in performing the measurements and recording them in a database.

- Emissions caused by start-up, shutdown and maintenance operations need to be taken into account. These depend heavily on the operating procedures. 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, a possible approach is to set up a measurement campaign to quantify the emissions linked to each operating step. However, because measurements can prove difficult to carry out for batch operations (because emissions might not be constant) calculations might be performed using methodologies such as the one contained in [229, US EPA 2007].

- Accidental emissions should not occur. Since they do happen, however, the related material (e.g. solvent) losses should be reflected in a material balance (see also Section 3.1.5.2.4). It is recommended that these incidents be tracked and a record kept of the estimated quantity emitted during each event.

Achieved environmental benefits
Waste gas emission quantification is used to derive strategies to tackle emissions to air in a more efficient way and finally achieve reductions in overall emissions to air.

Cross-media effects
No cross-media effects are considered to be of importance.

Operational data
No information provided.

Applicability
The technique is generally applicable.

Economics
No information provided.

Driving force for implementation
Reducing the environmental footprint of the installation as well as recovering valuable material are the main driving forces for the implementation of the technique.

Example plants
No information provided.

Reference literature
[13, CEFIC 1999] [29, US EPA 1995] [30, US EPA 1999] [79, US EPA 1995] [81, IMPEL 2000] [105, COM 2006] [113, COM 2006] [229, US EPA 2007]

3.2.3.2   Diffuse VOC emissions

The monitoring of diffuse VOC emissions is described in Sections 3.2.3.1, 3.5.4.4 and 3.5.4.5.

3.2.3.3   Odour emissions

The monitoring of odour emissions is described in Section 3.5.5.3.

3.3 Emissions to water

3.3.1 Water usage and waste water generation

3.3.1.1 Overview

Description

Some important – and normally easily retrofittable – production-integrated measures relevant to waste water are described below. 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 on other environmental compartments that might overshadow the benefits of water conservation or pollutant decrease.

Items to consider include:

- the knowledge and control of water consumption, by using water meters for example;
- the segregation of waste water streams (see Section 3.1.5.3.5.2);
- the development of strategies to minimise (fresh) water consumption and waste water arising in the production process(es) [98, Biener et al. 1999], 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. reuse 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 reuse (in the same or in another process), which results in the reduction of fresh water, waste water and load of contaminants;
    ◦ washing at high pressure and at a low flow rate;
    ◦ implementing multiple use and recirculation operations (see Section 3.3.1.4);
    ◦ using indirect cooling of vapour phases (see Section 3.3.1.5);
    ◦ using water-free vacuum generation (see Section 3.3.1.6);
    ◦ using solvents as the ring medium in vacuum pumps (see Section 3.3.1.7);
    ◦ closed-cycle liquid ring vacuum pumps (see Section 3.3.1.8);
    ◦ countercurrent product washing (see Section 3.3.1.12);
    ◦ using Cleaning-In-Place (CIP) systems;
- the challenge of waste gas abatement techniques (e.g. wet scrubbers, bioscrubbers, refrigerators with water cooling, wet cyclones, wet electrostatic precipitators) regarding their fresh water consumption and, if possible, avoiding it when the availability of fresh water is a limiting factor or when the receiving water is sensitive to disturbances (see Section 3.3.1.9).

The procedure for the reduction of water consumption and waste water generally follows the pathway illustrated in Figure 3.5.

As a first step, a balance of water and the main contaminants that might prevent its direct reuse is carried out (see Section 3.1.5.2.4). Some specific slightly contaminated process waters can be reused, e.g. rinsing water from ion exchangers (see Section 3.3.2.3.4.11) can be used in waste gas scrubbers (see Section 3.5.1.2.4). When the data collection from the waste water inventory/register (see Section 3.1.5.2.3) has not delivered consistent data, a subsequent data reconciliation is necessary, combined with additional elaborated measurements.

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 (see Section 7.3, Annex III for an example).
It must, however, not be overlooked that the enrichment of pollutants that cannot be removed by internal abatement or purification techniques may confine water reuse into water cycles.

* Associated with risk assessments to evaluate the impact of options on the industrial process
Source: Adapted from [98, Biener et al. 1999]
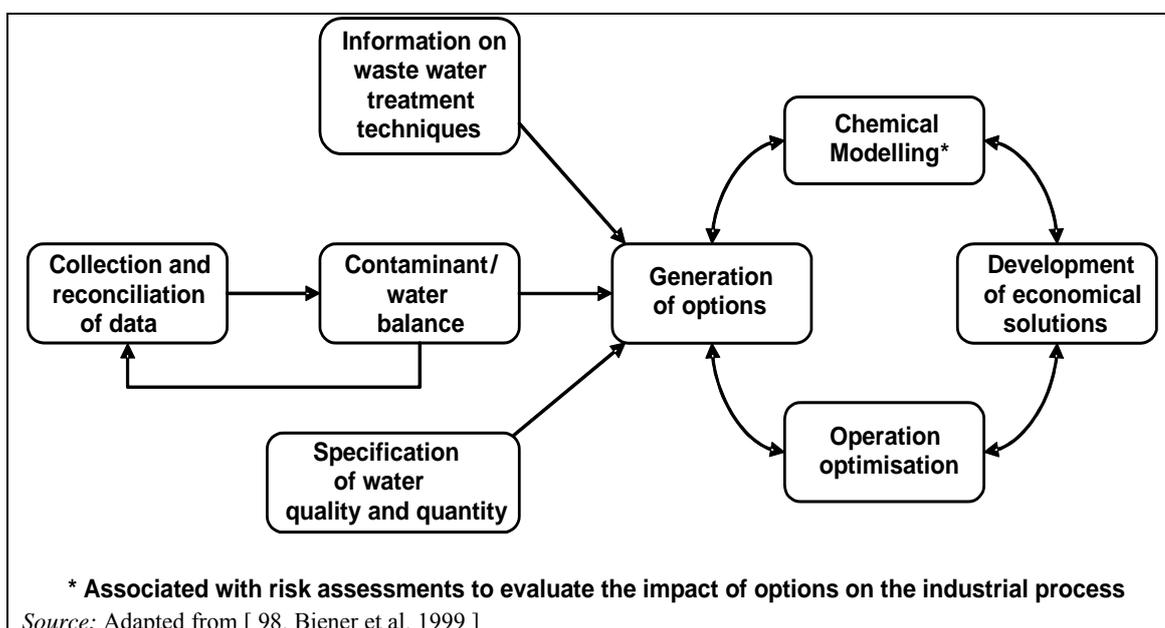
Figure 3.5:   General procedure to reduce water consumption and waste water

Achieved environmental benefits
The achieved environmental benefits include:

•   reduction of water consumption;
•   reduction of pollutants released to water;
•   by concentrating the pollutants in the waste water, the efficiency of treatment is increased.

Cross-media effects
There may be some cross-media effects depending on the concrete measures taken to reduce water usage (e.g. use of solvents, consumption of energy).

Recycling processes often generate risks for the quality of the recycled water (e.g. increase of the pollutant concentration). An upset in a waste water treatment process used prior to recycling may require another source of water to be used temporarily.

Operational data
No information provided.

Applicability
The reduction of water usage and waste water discharge is generally applicable.

Economics
No information provided.

Driving force for implementation
Reducing the environmental footprint of the installation as well as reducing costs are the main driving forces for the implementation of the technique.

Example plants
No information provided.

Reference literature
[98, Biener et al. 1999]

3.3.1.2 Countercurrent extraction

Description
Conventional product washing processes are multiple extractions working batch-wise by treating the product phase with water in order to remove salts or other minor soluble compounds. 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 countercurrent 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.

Achieved environmental benefits
Achieved environmental benefits of countercurrent extraction are:

- reduction of fresh water usage;
- reduction of the amount of waste water treated;
- more efficient treatment of pollutants and, potentially, material reuse/recycling.

Cross-media effects
Some raw materials and energy are consumed for the additional equipment and for pumping larger volumes compared to simple batch-wise extraction.

Operational data
The degree and method of optimisation depends on the production capacity and on the frequency of production runs.

Applicability
Countercurrent extraction 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.

Economics
Countercurrent extraction is cost-effective specifically for high-production plants or for plants producing high-value outputs.

Driving force for implementation
Cost benefits and reduction of water consumption.

Example plants
Example plants using countercurrent extraction can be found in the OFC sector [105, COM 2006].

Reference literature
[105, COM 2006]

3.3.1.3 Reactive extraction

Description
Organic acids can be selectively extracted from aqueous solutions after pH adjustment with a suitable organic base dissolved in hydrocarbons. The base can be for example a tertiary amine. The acid and base form a stable complex compound in the organic phase. After phase separation, the complex is split by the addition of aqueous NaOH and the acid can be obtained as a sodium salt. The base and hydrocarbons are used in a closed cycle.

Achieved environmental benefits
The achieved environmental benefits include:

- the recovery of valuable raw material or product;
- the reduction of organic waste water load.

Cross-media effects
No cross-media effects are believed to be likely.

Operational data
Operational data depend on the separation target.

Applicability
The technique is generally applicable for organic acids.

Other applications include

- phenols and bisphenols with 5 % trioctylamine in Shellsol AB;
- mercaptobenzothiazole with 20 % trioctylamine in Shellsol AB;
- metal cations with classic complexing/chelating agents.

Economics
The technique is lucrative/economically appealing if the recovered raw material or product is pure enough for further processing and waste water treatment costs are reduced.

Driving force for implementation
Driving forces for implementation include:

- the recovery of raw material or product;
- the reduction of waste water treatment costs;
- the reduction of waste water charges.

Example plants
No information provided.

Reference literature
[105, COM 2006].

3.3.1.4 Multiple use and recirculation operations

Description
A distinction has to be made here between waste water originating directly from production (e.g. reaction water, distillates, washing water, filtrates) and 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).

The reuse 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 the storage of waste water, which might be a limiting factor.

Other possibilities exist to recirculate effluents to the process instead of discharging them:

- rainwater can be collected and used for scrubber feed for example;
- recirculation of condensates.

Achieved environmental benefits
Achieved environmental benefits of the technique are:

- reduction of fresh water usage;
- reduction of the amount of waste water treated;
- material reuse/recycling.

Cross-media effects
Where effluent stream treatment is required for recirculation, this will result in additional energy and material consumptions (and costs) that could be large enough to negate the benefits of the eventual recirculation. Such an assessment will depend greatly upon local detailed circumstances.

Operational data
Specific treatment steps to remove interfering constituents can improve the efficiency of a recirculation operation. Thus, for example, neutralisation (see Section 3.3.2.3.2), stripping (see Section 3.3.2.3.4.17) or filtration (3.3.2.3.3.6) of process water streams can enable water to be reused, e.g. as raw water or utility water supply.

Applicability
The applicability of the technique largely depends on the specific production processes and the product specifications.

The reuse of process water (make-up water, mother liquors) is possible when constituents such as side products or salts do 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.

Multiple use and recirculation are usually much easier if the water is not in direct contact with the products.

Economics
Costs will increase if interim effluent treatment is required. Cost savings result from a lower fresh water use.

Driving force for implementation
Particular driving forces include:

- lack of availability of effluent discharge outlets, e.g. restricted by legislation or local circumstances;
- dry climates where water supply may be limited;
- economic aspects (e.g. due to lower charges/fees paid for fresh water use or due to product recovery and increase of product yield).

Example plants
Recycling of waste water after biological treatment and membrane filtration at a German plant producing polymers [106, COM 2007].

Reference literature
[106, COM 2007]

3.3.1.5   Indirect cooling of vapour phases

Description
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 prevents 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 [22, BMU/LAWA 2000] replacing only water lost by evaporation.

Achieved environmental benefits
Achieved environmental benefits of the technique are:

- reduction of the amount of waste water sent for treatment;
- reduction of fresh water usage.

Cross-media effects
Cross-media effects include energy consumption and replacement of water lost by evaporation.

Operational data
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.

Applicability
There are, however, processes where a conversion to indirect cooling is not appropriate [22, BMU/LAWA 2000] such as the cases given below.

- Where crystallisation stirs a liquid organic phase vigorously together with warm or hot water, and then the temperature is brought down 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.
- Where the diazotisation of amines is used, keeping the temperature 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.
- Where hot gas streams are quenched by the injection of cold water into the gas stream to decrease its temperature so effectively and rapidly that reactions in the gas stream are prevented (e.g. recombination reactions in flue-gas from combustion processes resulting in the generation of PCDDs/PCDFs) and simultaneously abating one of its pollutants (e.g. HCl).

Economics
No information provided.

Driving force for implementation
Using indirect cooling enables the saving of water and the reduction of the amount of waste water.

Example plants
No information provided.

Reference literature
[22, BMU/LAWA 2000]

3.3.1.6 Water-free vacuum generation

Description
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 [22, BMU/LAWA 2000]. In some cases, water-free vacuum generation can be achieved by use of the product as a barrier liquid in a mechanical vacuum pump, or by use of a gas stream out of the production process.

Achieved environmental benefits
Prevention of water contamination in vacuum generation is an achieved environmental benefit of water-free vacuum generation.

Cross-media effects
In selecting the proper process for water-free vacuum generation, account needs to be taken of the potential problems, particularly with respect to corrosion, tendency to cake, explosion risk, plant safety and operational reliability.

Operational data
No information provided.

Applicability
Whether water-free vacuum generation is possible has to be determined in each particular case. 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, e.g. by 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 (e.g. water vapour), dust-forming or coating material. The use of dry running pumps is restricted when the gas stream contains corrosive substances and it is also usually restricted to some temperature classes.

Economics
A dry vacuum pump investment is much higher than that of a water ring vacuum pump but on a long-term basis the total cost can be balanced because of the cost to treat the liquid ring water.

As an example, at an OFC plant, three water ring pumps were replaced by two new dry running vacuum pumps. Operating costs of the old and the new installation are shown in the OFC BREF. The investments in the new vacuum generation technique including safety equipment and installation were net EUR 89 500 (DEM 175 000 in 1999; fixed currency conversion rate from January 1999 onwards: EUR/DEM = 1.956). The payback time is thus one year [105, COM 2006].

Driving force for implementation
Reduction of waste water loads and cost savings are the driving forces for implementation of this technique.

Example plants
OFC plant [105, COM 2006].

Reference literature
[22, BMU/LAWA 2000] [105, COM 2006]

3.3.1.7 Liquid ring vacuum pumps using solvents as the ring medium

Description
When a single (and not highly volatile) solvent is pumped, a liquid ring pump using the same solvent as the medium can be applied in combination with a solvent recovery system. Besides the avoidance of potential water contamination, the usage of solvents as the ring medium shows other advantages:

- the vacuum is maintained by cooling, which is restricted in the case of water to values above 0 °C but is more flexible if a solvent with a lower melting point is chosen;
- a better vacuum can be achieved by using solvents with a lower vapour pressure than water.

Achieved environmental benefits
Prevention of water contamination in vacuum generation is the environmental benefit of this technique.

Cross-media effects
No cross-media effects are believed to be likely.

Operational data
The use of toluene as the ring liquid and the treatment of waste gases from condensers by thermal oxidation were reported for an OFC plant [105, COM 2006].

Energy use for cooling and steam generation. In comparison to a plain dry running vacuum pump, additional treatment of the waste gas may be required.

Applicability
This technique is generally applicable. The reuse of recovered solvents may be restricted in the manufacturing of active pharmaceutical ingredients and of explosives.

In the example given, the water from the stripping column is forwarded to the WWTP. In other cases, the characterisation of such water may lead to other options.

As a rule of thumb, the stripping process is economically feasible only for more than 1 000 kg of solvent per year.

Economics
No comparison of costs was possible for the conventional ring pump compared to the solvent ring pump due to data not being provided, but economic advantages are assumed to be the main driving force. Where solvents cannot be reused, the economic benefit will be limited.

Driving force for implementation
Reduction of waste water loads and economics are the driving forces for the implementation of this technique.

Example plants
OFC plant [105, COM 2006].

Reference literature
[105, COM 2006]

3.3.1.8 Closed-cycle liquid ring vacuum pumps

Description
Liquid ring vacuum pumps can be designed for total recirculation of the sealing liquid. The system normally includes a pump suction condenser with a condensate recovery tank and a post condenser for the condensation of residual gas. The construction materials are normally CrNiMo stainless steel and all process side-related seals are made of PTFE.

Achieved environmental benefits
Achieved environmental benefits of the technique are:

- a highly reduced amount of sealing liquid (e.g. water) becomes contaminated;
- a completely closed system with no contact between the cooling and the sealing liquid;
- handled gases/vapours (e.g. solvents) are recovered.

Cross-media effects
No cross-media effects are believed to be likely.

Operational data
The recirculated sealing liquid should be considered for disposal after a certain time.

Applicability
This technique is widely applicable.

The reuse of recovered solvents may be restricted in the manufacturing of APIs, but not applicable for the manufacturing of explosives due to safety concerns.

Economics
No information provided.

Driving force for implementation
The reduction of waste water loads, and economics are the driving forces for the implementation of this technique.

Example plants
OFC plants [105, COM 2006].

Reference literature
[105, COM 2006]

3.3.1.9 Water-free processes for waste gas treatment

Description
About one third of the waste gas treatment 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.

Examples of waste water-free techniques for waste gas cleaning include:

- the collection and subsequent thermal or catalytic oxidation of calorific waste gas streams, preferably with energy recovery (see Sections 3.5.1.3.5 and 3.5.1.3.6);
- the application of appropriate dry dedusting equipment (e.g. demisters, cyclones, electrostatic precipitators and fabric filters) to separate particulates and aerosols (see Section 3.5.1.4);

- the use of dry/semi-dry gas treatments (e.g. activated carbon adsorption, see Section 3.5.1.2.3, lime/sodium bicarbonate injection, see Section 3.5.1.5.2) for waste gas streams loaded with organic or inorganic gaseous contaminants;
- use of regenerative organic solvents (or oils) instead of water as a scrubbing liquid for specific gaseous contaminants.

Achieved environmental benefits
Avoiding or reducing the amount of waste water sent to treatment and reducing the consumptions associated with waste water treatment are the environmental benefits of the technique.

Cross-media effects
Use of materials (e.g. solvents, activated carbon) depending on the specific water-free technique used. Some of the water-free techniques might be more energy-intensive and result in the generation of more solid waste.

Operational data
No information provided.

Applicability
Water-free techniques for waste gas cleaning are used, in particular, when hazardous substances or non-biodegradable organic substances would otherwise enter a biological waste water treatment plant, where they might cause disturbances or be discharged untreated into the receiving water.

Economics
Where solid waste disposal costs are high there may be benefits in adopting wet flue-gas treatment owing to the reduced solid waste arising.

Driving force for implementation
Reduction of waste water loads is a driving force for implementation. The lack of availability of a water discharge outlet is a key driver.

Example plants
Zero-effluent flue-gas cleaning systems are widely used throughout Europe, e.g. in the chemical industry and incineration sectors.

Reference literature
No reference literature provided.

3.3.1.10 Substance recovery from mother liquors and substance retention or by optimised processes

Description
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.:

- the 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 the recovery of chlorine (from chlorinated organic compounds) as hydrochloric acid.

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

Substance retention by 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.

Achieved environmental benefits
Achieved environmental benefits of the technique are:

- reduction of the amount of waste water treated;
- material reuse/recycling.

Cross-media effects
None.

Operational data
No information provided.

Applicability
Generally applicable.

Economics
No information provided.

Driving force for implementation
Substance recovery is both economically beneficial as well as environmentally desirable.

Example plants
No information provided.

Reference literature
No reference literature provided.

3.3.1.11 Use of slightly contaminated raw materials and auxiliaries

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

- 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;
- the increase of contaminant importation because of recycled materials;
- the transfer of emission problems to other locations by work-up of the raw material.

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

Achieved environmental benefits
The substitution or elimination of some of the raw materials used in the production of chemicals can result in the combination of the following benefits:

- a reduction in the amount of waste generated;
- a reduction in emissions to air;
- a reduction in emissions to the receiving water.

Cross-media effects
The use of energy and materials for purifying the raw materials (if required) are the cross-media effects. It should be evaluated on a case-by-case basis whether the reduction/elimination of side products/contaminants is more desirable on the manufacturer's or on the user's side.

Operational data
No information provided.

Applicability
Applicability depends, in particular, on the cost of the substitute raw materials purchased, or on the cost of the purification equipment needed at the installation to purify the feedstock.

The substitution of raw materials may not be possible, notably in the production of explosives and ammonium nitrate-based fertilisers, because known impurities can be of paramount importance in obtaining the required product under all security and safety conditions (e.g. effect on shape and size of crystals).

Economics
Economic factors include the cost of installing and running the purification equipment at the site (if purification equipment is required). Using feedstock with lower impurities might be more expensive, depending on market conditions.

Cost savings in the treatment of waste may result from the substitution or elimination of some of the raw materials used. However, this may be more than balanced by the increased costs of a purer raw material.

Driving force for implementation
The use of slightly contaminated raw and auxiliary materials is an important technique for the prevention of emissions.

Example plants
Many installations of several industrial sectors use the technique.

Reference literature
[107, COM 2007]

3.3.1.12 Countercurrent product washing

Description
As a polishing step, chemical products are often washed with an aqueous phase in order to remove impurities. High efficiencies in combination with low water consumption (and low waste water generation) can be achieved with countercurrent washing, which may also be combined with other purification steps. The degree of optimisation of the washing process depends on the production level and regularity.

Achieved environmental benefits
The achieved environmental benefits include:

* lower water consumption;
* less waste water is created;
* recycling or individual treatment of portions of particular contents or concentrations.

Cross-media effects
No cross-media effects are believed to be likely.

Operational data
No information provided.

Applicability
The technique is widely applicable. It is especially economical in larger scale plants, since it can be tailored specifically to a production process. For small amounts, experimental production runs, and short or rare production campaigns, these processes cannot be used.

Economics
No information provided.

Driving force for implementation
Cost benefits and reduction of water consumption are the driving forces for using the technique.

Example plants
OFC plant [105, COM 2006].

Reference literature
[105, COM 2006]

3.3.2 Individual waste water treatment techniques

3.3.2.1 Equalisation

Description
In general, waste water treatment plants (WWTPs) (especially biological ones) operate most effectively at reasonably constant conditions of certain parameters, especially pH, hydraulic load (or flow rate) and contaminant load/concentrations.

To buffer the production against short-term (e.g. daily) and long-term (e.g. weekly) variations, equalisation facilities are put in place, either decentralised at the various production sites or centrally in or near the final WWTP.

Furthermore, unusual influxes into the WWTP resulting from operational failures are controlled by additional centralised retention capacity. The timely detection of such unusual events is necessary. The buffering and retention volumes also allow operators to check the compatibility of the waste water influent with the subsequent treatment. Flow and load/concentration balancing are also referred to as equalisation, buffering or homogenisation.

Although equalisation is frequently achieved by using central or decentralised tanks, it may also be (partially) achieved by other management techniques (e.g. planning of production activities).

Achieved environmental benefits
This technique allows a more efficient use of subsequent waste water treatments (e.g. WWTP) and therefore lowers emissions to the receiving water.

The result of buffering and equalising can include:

- equalisation of loads, such as:
  ◦ organic load;
  ◦ salt concentrations, especially if salt concentrations are about or more than 10 g/l;
  ◦ 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 (see Section 3.3.2.3.2);
- equalisation of waste water flow rate.

Cross-media effects
None.

Operational data
The appropriate capacity of the equalisation tank is a function of the anticipated fluctuations [251, Ullmann's 2000].

Flow and load balancing is also used as a control measure for unusual influx events to the WWTP, and so the capacity of the equalisation tank is determined not only by the fluctuations, as mentioned above, but also by the extent of the hazard potential.

In practice, both flow rate and contaminant loads/concentrations can fluctuate markedly due to factors such as:

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

The equalisation tank 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 be emitted to the environment, tanks are used for this purpose, whereas for surface water drainage, open lagoons or retention ponds are used (see Section 3.3.2.3.6.2). If the retention time in the equalisation tank is long, then some reactions may take place in the waste water that can lead to odour problems, foam production and precipitation of solids.

Table 3.6 presents examples of the buffering capacities in place at some German chemical sites.

Table 3.6: **Examples of buffering capacities at some German chemical sites**

WWTP No	Flow of influent to WWTP	Capacity for mixing and equalising the input to the chemical-mechanical stage	Buffering capacity between chemical-mechanical stage and biological stage	Retention capacity for operational failures
WWTP 1	8 000 m^3/d	80 m^3	20 000 m^3	10 000 m^3 (+ 900 m^3)
WWTP 2	10 000 m^3/d	300 m^3	2 × 4 800 m^3	2 × 3 000 + 390 m^3
WWTP 3	6 000 m^3/d	NI	NI	23 000 m^3
WWTP 4	8 500 m^3/d	NI	3 000 m^3	12 000 m^3
WWTP 5	10 000 m^3/d	1 500 m^3	4 000 m^3	9 500 m^3
WWTP 6	65 000 m^3/d	NI	40 000 m^3	28 000 m^3
WWTP 6	45 000 m^3/d	NI	15 000 m^3	47 500 m^3
WWTP 7	315 000 m^3/d	NI	NI	60 000 m^3
WWTP 8	3 800 m^3/d	NI	18 000 m^3	11 500 m^3
WWTP 9	34 000 m^3/d	NI	2 400 m^3	11 600 m^3
NB: NI = no information provided.				
Source: [217, RP Freiburg 2009]				

Bypassing equalisation facilities, as shown in Figure 3.7, for maintenance purposes or in case of pollution detected inside the tanks is possible. This means that the treatment chain is able to operate normally without the equalisation capacity or with reduced equalisation capacities if there are several capacities.

Applicability
This technique is generally applicable. It is mostly applicable when production output is irregular, for example when industries are governed by specific campaigns (e.g. production of speciality or fine chemicals).

Economics
The cost of buffering is primarily determined by the size of the tank, placement and the materials used. In general, one should consider a cost of EUR 100/m^3 for a concrete tank, excluding accessories and placement. Buffer tanks made of other materials are normally more expensive, e.g. an enclosed 100 m^3 polyester buffer tank with stirrer costs EUR 50 000 [63, VITO 2010].

Driving force for implementation
Compliance with legal requirements to limit pollution to receiving waters is the driving force for the implementation of this technique.

Example plants
Virtually all WWTPs. Examples of chemical sites using the technique are mentioned under operational data above.

Reference literature
[63, VITO 2010] [217, RP Freiburg 2009] [251, Ullmann's 2000]

3.3.2.2   Buffer storage for waste water incurred during other than normal operating conditions

Description
Other than normal operating conditions such as 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 [251, Ullmann's 2000].

Achieved environmental benefits
The technique allows for lower emissions to the receiving water.

Cross-media effects
There are no cross-media effects associated with this technique.

Operational data
There are several buffer devices available. 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 and load balancing tanks (see Section 3.3.2.1).

The appropriate buffer storage capacity is usually based on a risk assessment (taking into account e.g. the nature of the pollutant, the effects on further treatment, and the receiving environment.

One device (see Figure 3.6), the self-contained buffer, contains two buffer tanks that receive the waste water stream alternately. While one tank is filled, the content of the other is checked and then released to the waste water discharge or downstream of the WWTP or disposed of as waste, depending on the results of the check. The receiving capacity of each containment needs to be sufficient to hold the entire amount of waste water arising during the period of analysis and the emptying 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 emptying time and vice versa, which might result in a vicious circle.

Another device is the connected buffer, either discontinuously (see Figure 3.7) or continuously filled (see Figure 3.8). The discontinuously filled 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.
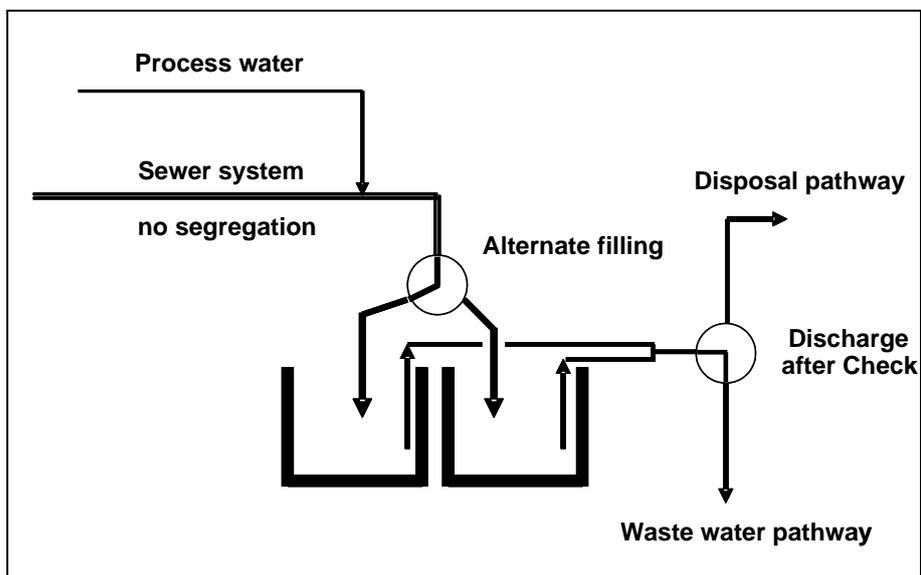
Figure 3.6: Self-contained buffer with alternative filling
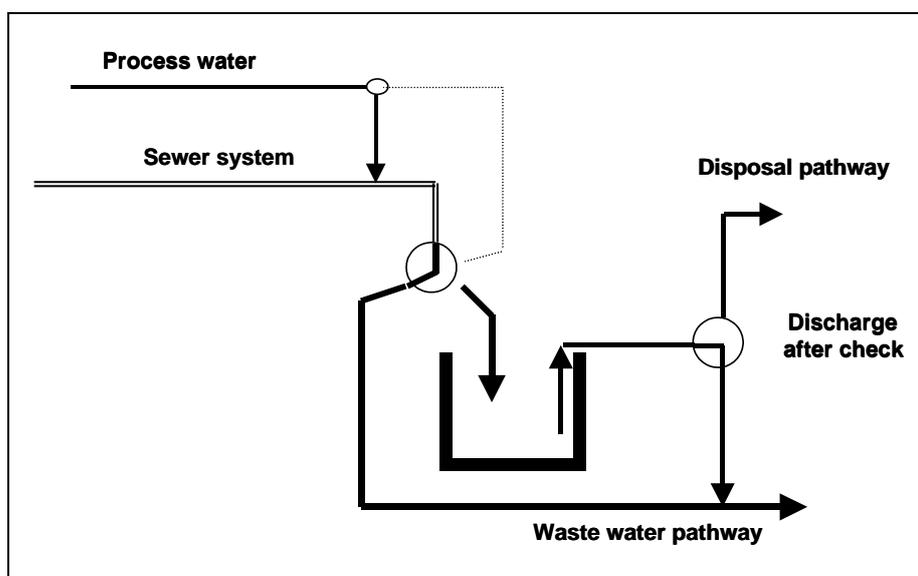
Figure 3.7: Connected buffer, discontinuously filled

The continuously filled connected buffer can also be used as an equalisation or flow balancing tank (see Section 3.3.2.1). A control and alarm system ensures 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 emptied.
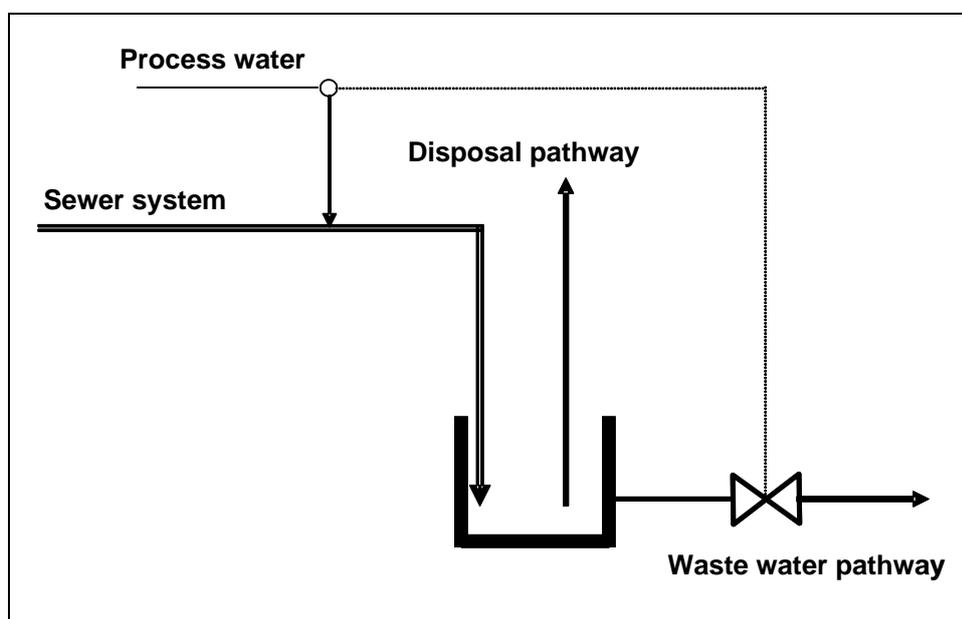
Figure 3.8: **Connected buffer, continuously filled**

A further system (see Figure 3.9) is suited to receive and buffer leakage losses, with leakages collected in a separate sewer. Such a sewer is used as a drainage system for potentially polluted outdoor areas, e.g. with 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.
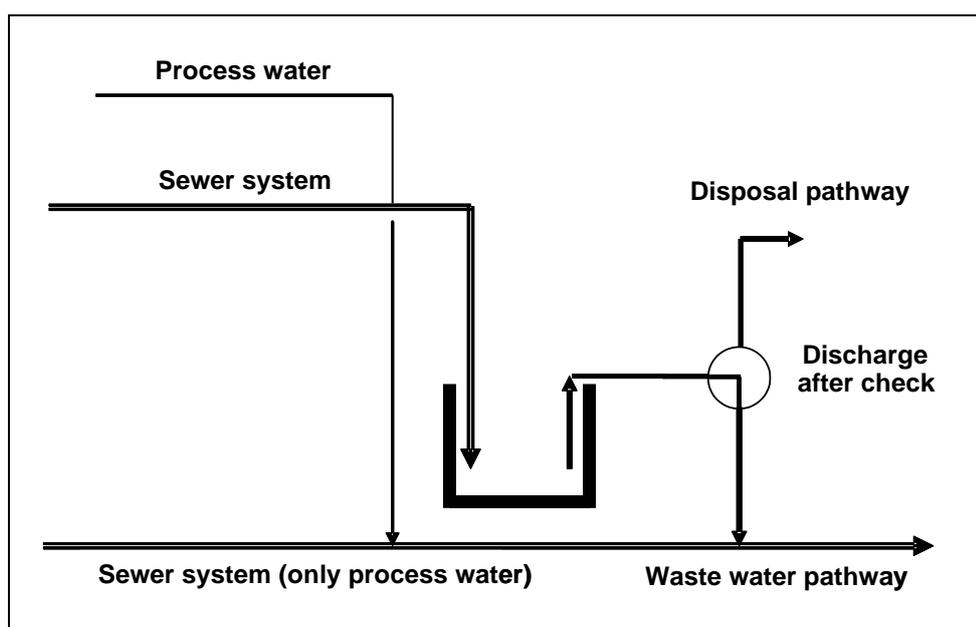
Figure 3.9: **Leakage buffer system**

Applicability
The interim storage of contaminated rainwater requires segregation, which may not be applicable in the case of existing waste water collection systems.

Economics
The cost of buffering is primarily determined by the size of the tank, placement and the materials used. In general, one should consider a cost of EUR 100/m^3 for a concrete tank, excluding accessories and placement. Buffer tanks made of other materials are normally more expensive, e.g. an enclosed 100 m^3 polyester buffer tank with stirrer costs EUR 50 000 [63, VITO 2010].

Driving force for implementation
Compliance with legal requirements to limit pollution to receiving waters is the main driving force for implementation of the technique.

Example plants
Virtually all WWTPs apply the technique. Examples of chemical sites using the technique are mentioned in Table 3.6.

Reference literature
[63, VITO 2010] [217, RP Freiburg 2009] [251, Ullmann's 2000]

3.3.2.3   End-of-pipe techniques

3.3.2.3.1   Overview

To introduce a logical order in the description of treatment techniques, the relationship between the pollutant and respective typical treatment technique is taken as the reference, as pointed out in Section 1.6.3.2 and illustrated in Figure 3.10. Table 1.1 lists the main waste water end-of-pipe treatment techniques and the pollutant(s) targeted for abatement by each technique. The details of the applicability of each technique are given in the specific sections as indicated in Table 1.1.

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 3.3.2.3.3.2, sedimentation – see Section 3.3.2.3.3.4, oil-water separation – see Section 3.3.2.3.3.8);
- flotation (see Section 3.3.2.3.3.5);
- filtration (filtration – see Section 3.3.2.3.3.6, membrane filtration – see Section 3.3.2.3.3.7).

These separation techniques 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.
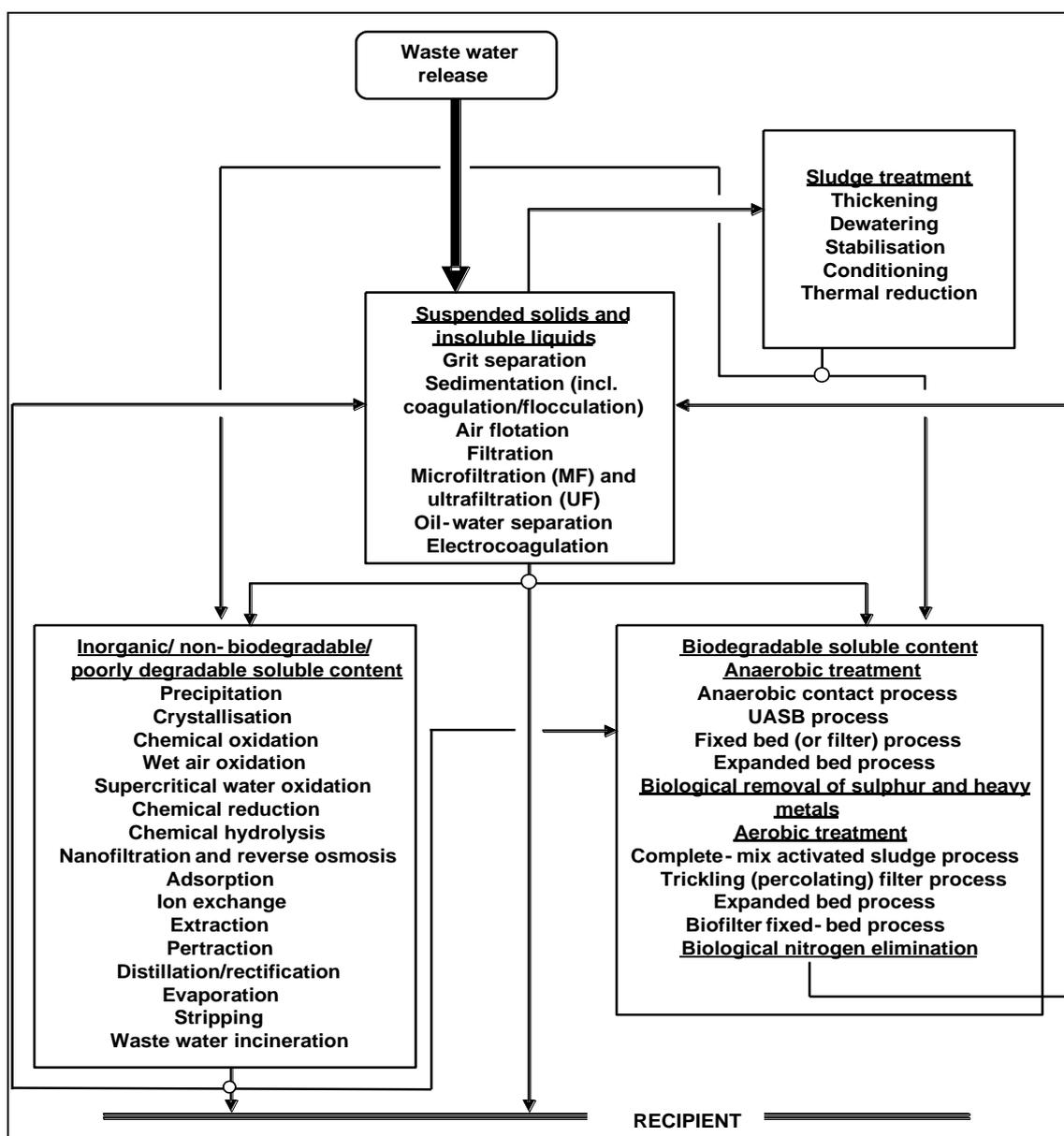
Figure 3.10: Range of waste water treatment techniques in relation to type of contaminants

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. Biodegradable compounds are compounds that are subject to degradation by means of a biological activity. Refractory COD/TOC and heavy metals are examples of non-biodegradable compounds.

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 3.3.2.3.4.2);
- crystallisation (see Section 3.3.2.3.4.3);
- chemical reactions (chemical oxidation – see Section 3.3.2.3.4.4, wet air oxidation – see Section 3.3.2.3.4.4.3, supercritical water oxidation – see Section 5.1.4, chemical reduction – see Section 3.3.2.3.4.5 and chemical hydrolysis – see Section 3.3.2.3.4.6);
- membrane 'filtration' (nanofiltration and reverse osmosis, see Section 3.3.2.3.4.7);
- adsorption (see Section 3.3.2.3.4.10);
- ion exchange (see Section 3.3.2.3.4.11);

- extraction (see Section 3.3.2.3.4.12);
- distillation/rectification (see Section 3.3.2.3.4.14);
- evaporation (see Section 3.3.2.3.4.15);
- stripping (see Section 3.3.2.3.4.17);
- incineration (see Section 3.3.2.3.4.18).

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

The following substances/substance groups are relevant in practice as examples for insufficient elimination in central biological WWTPs at chemical sites:

- chelating agents such as EDTA and DTPA;
- cyclic ethers, particularly dioxanes;
- oligomers in waste water streams from the production of polyacrylonitrile;
- oligomers in waste water streams from the production of methylcellulose;
- diglyme;
- intermediates from the production of optical brighteners, e.g. dinitrosalicylic acid;
- side products and products from the production of optical brighteners (e.g. triazine derivatives);
- iodinated X-ray contrast media, such as diatrizoic acid, iopamidol;
- some organic dyes;
- PFOS and other perfluorinated compounds;
- MTBE.

In most cases, and contrary to products (single substances), (many) side products or auxiliaries are a matter of concern in the waste water stream.

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 treatment (anaerobic contact process, UASB process, fixed-bed process, expanded-bed process – see Section 3.3.2.3.5.2 – and biological removal of sulphur compounds and heavy metals – see Section 3.3.2.3.5.3);
- aerobic treatment, (complete mix activated sludge process, membrane bioreactor process, trickling filter process, expanded-bed process, fixed-bed biofilter process – see Sections 3.3.2.3.5.4, 3.3.3.1, and 3.3.3.2);
- nitrification/denitrification (see Section 3.3.2.3.5.5).

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, 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 site.

Sludge treatment techniques may include:

- thickening (see Section 3.4.2.2);
- dewatering (see Section 3.4.2.2);
- stabilisation (see Section 3.4.2.3);
- conditioning (see Section 3.4.2.3).

3.3.2.3.2   Neutralisation

Description
Neutralisation is the process by which the pH of the incoming waste water is adjusted to the neutral pH level (approximately 7) by the addition of chemicals so as to make it biologically treatable in the waste water treatment plants and also to make it comply with the discharge standards. In principle, all types of waste water can be neutralised, but the amount of chemicals needed for the neutralisation process may vary greatly because of the buffer capacity of the waste water. Buffer capacity reflects the resistance of the waste water against a pH change and is caused by the presence of (hydrogen) carbonate, (hydrogen) phosphates, (hydrogen) sulphide and silicates. For neutralising waste waters, in general, sodium hydroxide (NaOH) or calcium hydroxide ($Ca(OH)_2$) is used to increase the pH; whereas, sulphuric acid (H_2SO_4), hydrochloric acid (HCl) or carbon dioxide (CO_2) is used to decrease the pH.

Achieved environmental benefits
Emissions of acids and alkalis to water are reduced. Moreover, biological treatment efficiency and thus effluent quality are increased as the biological processes are adversely affected by extreme pH levels and fluctuations.

Cross-media effects
Acids or alkalis are consumed. Neutralisation leads to increased salt concentrations in treated waste water (e.g. chloride, sulphate). The consumption of chemicals and the generation of salts can be reduced by mixing acidic and alkaline waste water streams before central neutralisation (i.e. equalisation, see Section 3.3.2.1).

Waste waters containing particular types of salts may result in the release of toxic gases upon the addition of neutralisation chemicals which can present a risk to health and the environment.

Operational data
Neutralisation can be performed in one or two stages. A two-stage neutralisation at the beginning of the WWTP was reported for WWTP #16, the first stage with the addition of hydrochloric acid and the second stage with lime [222, CWW TWG 2013].

Applicability
Neutralisation is applicable to waste waters originating from almost all types of industrial activities. However, in particular cases, neutralisation can drastically alter the composition of the waste water. Generally, inorganic acids/bases are used for neutralisation which might result in the formation of potentially insoluble salts. The choice of chemicals used (acids/alkalis) for neutralisation must also be compatible with the desired result.

Economics
The investment costs for the installation of a neutralisation process are very low compared to the total investment costs of the waste water treatment plant. The equipment consists of storage tanks, reaction tanks, dosage and mixing units. The operating costs depend on the characteristics of the waste water (pH, buffer capacity) as it will affect the amount of chemicals used for neutralisation.

Driving force for implementation
Legal requirements. To improve the biological treatability of the waste water in the WWTP.

Example plants
Neutralisation is one of the most frequently used treatment techniques reported in the questionnaires (see Section 2.2).

Reference literature
[63, VITO 2010] [222, CWW TWG 2013]

3.3.2.3.3   Insoluble contaminants/mechanical separation

3.3.2.3.3.1   Overview

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 can usually be treated to get rid of them by separation processes as described below.

3.3.2.3.3.2   Grit separator

Description
Grit separation is the removal of sand and gravel from rainwater. Grit chambers are used for this purpose because the sand might otherwise be deposited into inconvenient places, disturbing the treatment process and leading to rapid abrasion in the pumps [251, Ullmann's 2000].

Grit chambers are part of the WWTP and are usually situated immediately downstream of 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 [251, Ullmann's 2000]:

- channel-shaped horizontal-flow grit chambers, which maintain the required flow rate in combination with a Venturi flume, suitable for highly fluctuating waste water streams (see Figure 3.11);

Source: [251, Ullmann's 2000]
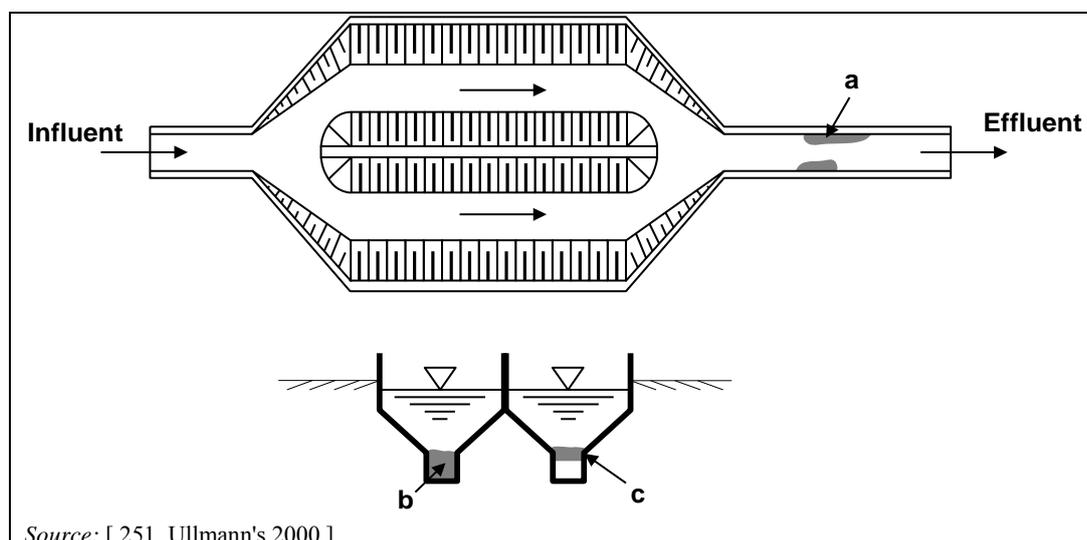
Figure 3.11:   Channel-shaped horizontal-flow grit chamber

- circular grit chambers, where the water is introduced tangentially, causing the content to circulate and the sand to be washed to the centre to be removed by an air-jet lift; this chamber type is less suitable for highly fluctuating flow rates (see Figure 3.12);

Source: [251, Ullmann's 2000]
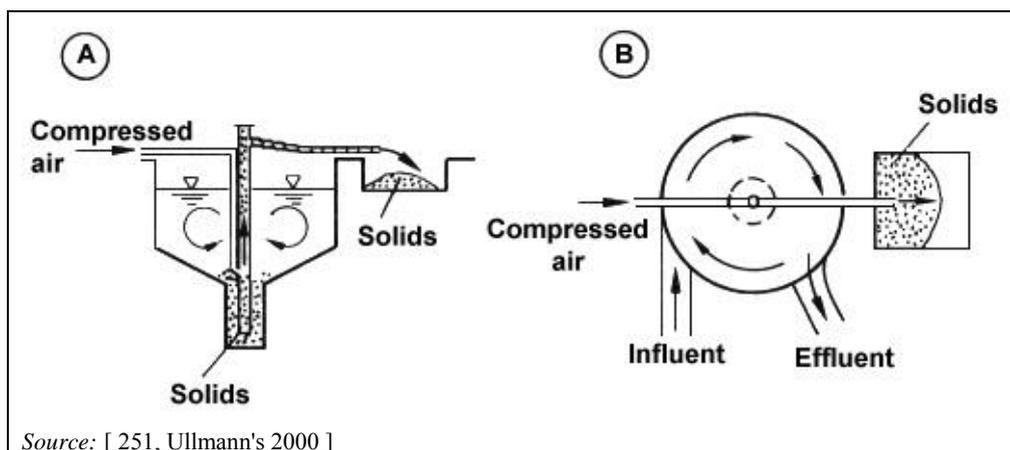
Figure 3.12: Circular grit chamber

- aerated grit chambers, 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 causes no problems with fluctuating flow rates (see Figure 3.13) [251, Ullmann's 2000].

Source: [251, Ullmann's 2000]
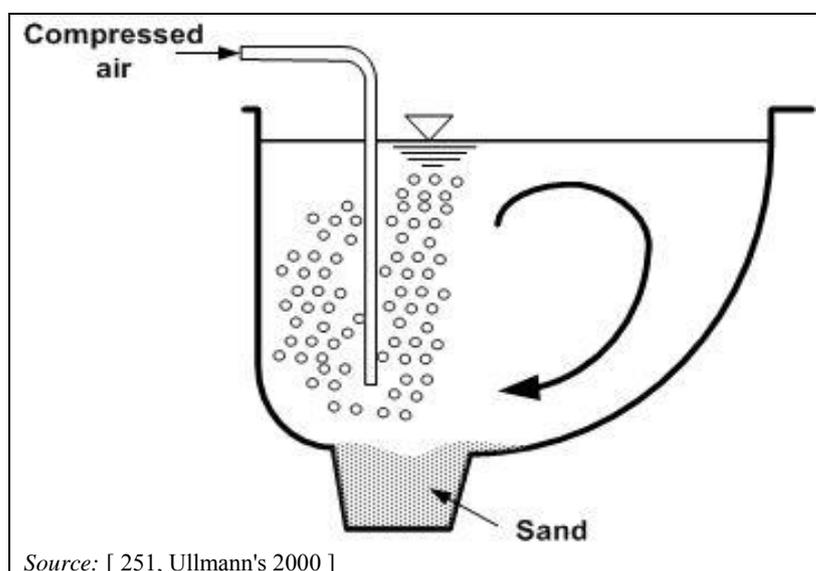
Figure 3.13: Aerated grit chamber

Storage facilities for the separated sand are necessary until it is discharged.

Achieved environmental benefits
Grit chambers are not installed for environmental protection reasons but to protect downstream equipment from wear and from blockages.

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

Electricity is consumed 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 from the main plant, depending on the kind of waste water being treated. Enclosing the equipment might be necessary.

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

Applicability
Grit chambers are used when the WWTP also has to deal with rainwater, which normally entails a considerable amount of sand [251, Ullmann's 2000]. Grit separation of solids is essential to protect downstream equipment.

Application limits and restrictions are given in Table 3.7.

Table 3.7: Application limits and restrictions associated with grit separation of solids

Issue	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

Economics
No information provided.

Driving force for implementation
The driving force for implementation of the technique is the protection of the downstream waste water treatment units.

Example plants
Nearly all waste water treatment plants use the technique.

Reference literature
[251, Ullmann's 2000]

3.3.2.3.3.3   Coagulation and flocculation

Description
Coagulation and flocculation occur in successive steps which are intended to overcome the forces stabilising the suspended particles, allowing particle collision and growth of floc.

Coagulation is the first step. It aims at destabilising the particles' charge by neutralising their electrical surface charge. This is carried out by adding coagulants with charges opposite to those of the suspended solids to the waste water. This allows the particles to stick together into slightly larger particles. Common coagulant chemicals used include alum, ferric sulphate, ferric chloride, ferrous sulphate, aluminium chloride, polyaluminium chloride and sodium aluminate. The first four will lower the alkalinity and pH of the solution while the sodium aluminate will add alkalinity and raise the pH. Polymers (anionic or cationic) are becoming more widely used as coagulant aids together with the conventional inorganic coagulants.

If solids are being coagulated, a high-energy, rapid mix to properly disperse the coagulant and promote particle collisions is needed to achieve good coagulation. Over-mixing does not affect coagulation, but insufficient mixing will leave this step incomplete. Coagulants should be added

where sufficient mixing will occur. Proper contact time in the rapid-mix chamber is typically one to three minutes. If liquids are being coagulated, a high-energy mix is not necessary as long as there is sufficient contact time to ensure good dispersion mixing. Also, for liquids, this can be achieved in a flow line rather than a tank.

Flocculation is a gentle mixing stage which aims at increasing the particle size. Collisions of microfloc particles cause them to bond to produce larger flocs. This occurs in the presence of inorganic (formed by the coagulant) or added organic polymers. Contact times for flocculation range from 15 or 20 minutes to an hour or more.

Once the floc has reached the optimum size and strength, the waste water can be brought to sedimentation (see Section 3.3.2.3.3.4).

Flocculation requires careful attention to the mixing velocity and amount of mix energy. To prevent the floc from tearing apart or shearing, the mixing velocity and energy input are usually tapered off as the size of the floc increases. Once flocs are torn apart, it is difficult to get them to re-form to their optimum size and strength. The amount of operator control possible in flocculation is highly dependent upon the type and design of the equipment. If liquids are being coagulated, using a flow line rather than a tank for carrying out the mixing also prevents the floc from tearing apart or shearing.

Achieved environmental benefits
Coagulation and flocculation are used to separate suspended solids from waste water.

Cross-media effects
The consumption of auxiliary materials (i.e. coagulant) and the use of energy for mixing are the main cross-media effects associated with the use of the technique.

Operational data
The effectiveness of coagulation and flocculation and selection of the coagulants depend upon understanding the interaction between the charge, size, shape and density of the particles to be separated. Final selection of the coagulant(s) should be made following thorough jar testing and plant-scale evaluation. Considerations must be given to required effluent quality, effect on downstream treatment process performance, cost, method and cost of sludge handling and disposal, and overall net cost at the dose required for effective treatment.

Applicability
The technique is generally applicable to waste waters loaded with suspended solids.

Economics
The operating costs of a coagulation and flocculation process are mainly due to the use of chemicals. The choice of chemicals and the required dosage depend greatly on the waste water to be treated. The cost of chemicals is reported to be in the range of EUR 0.15–5 per kg (chemical dosage is usually in the range of 0.5–100 mg/l). The removal cost of the sludge is around EUR 500 per tonne of dry matter. Other operating costs include costs of energy, maintenance and personnel [63, VITO 2010].

Driving force for implementation
The main driving force for implementing the technique is to enable an efficient settling and removal of solids in a successive sedimentation treatment (see Section 3.3.2.3.3.4).

Example plants
Sectors where coagulation/flocculation is applied include: the chemical industry, the textile industry, the food industry, slaughterhouses, and in the surface treatment of metals.

Reference literature
[1, Metcalf and Eddy 1991] [63, VITO 2010]

3.3.2.3.3.4   Sedimentation

Description
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 and their density is too close to that of water or they form colloids, special chemicals are added to cause the solids to settle, such as:

- aluminium sulphate (alum);
- ferric sulphate;
- ferric chloride;
- lime;
- polyaluminium chloride;
- polyaluminium 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 and oil in waste water) and emulsions entrapping solids (coagulation) and/or the agglomeration of these particles into 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 3.8. The removal levels in this table, however, should not be confused with the achievable performance of a treatment technique.

Table 3.8:   Removal of waste water contaminants under the influence of coagulation

Pollutant	Abatement efficiency ([1]) (%)
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
([1]) The abatement efficiencies are indicative and depend on the specific operating conditions (e.g. pH, type and dose of coagulant used) and on the feed concentration of pollutant(s). *Source:* [3, Environment Agency (England and Wales) 1997]	

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 1.5 hours to 2.5 hours (see Figure 3.14 as an example of a circular tank);

Source: [1, Metcalf and Eddy 1991]
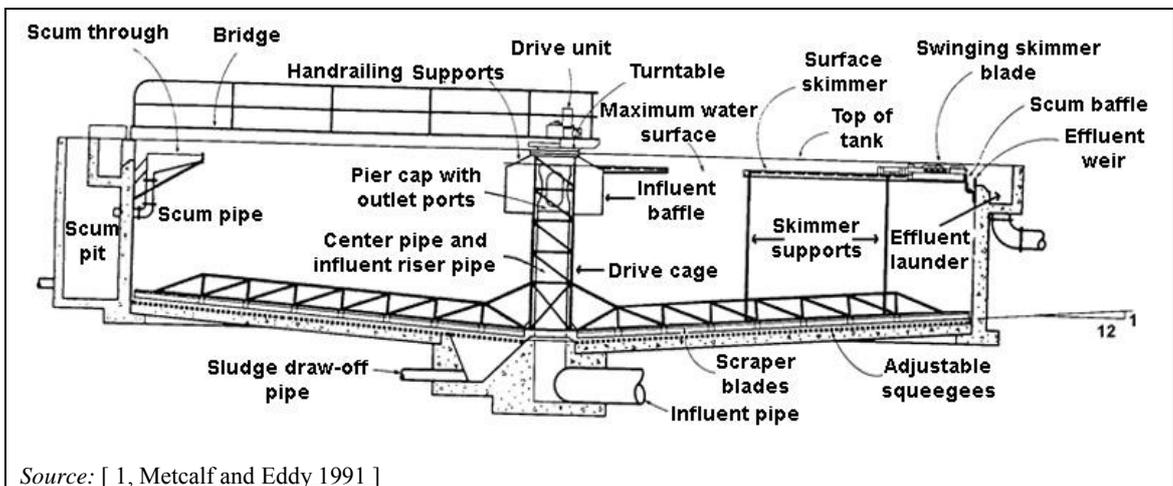
Figure 3.14: Circular sedimentation or settler tank

- hopper-bottom tanks, with vertical flow, usually not equipped with mechanical sludge removal systems (see Figure 3.15);

Source: [251, Ullmann's 2000]
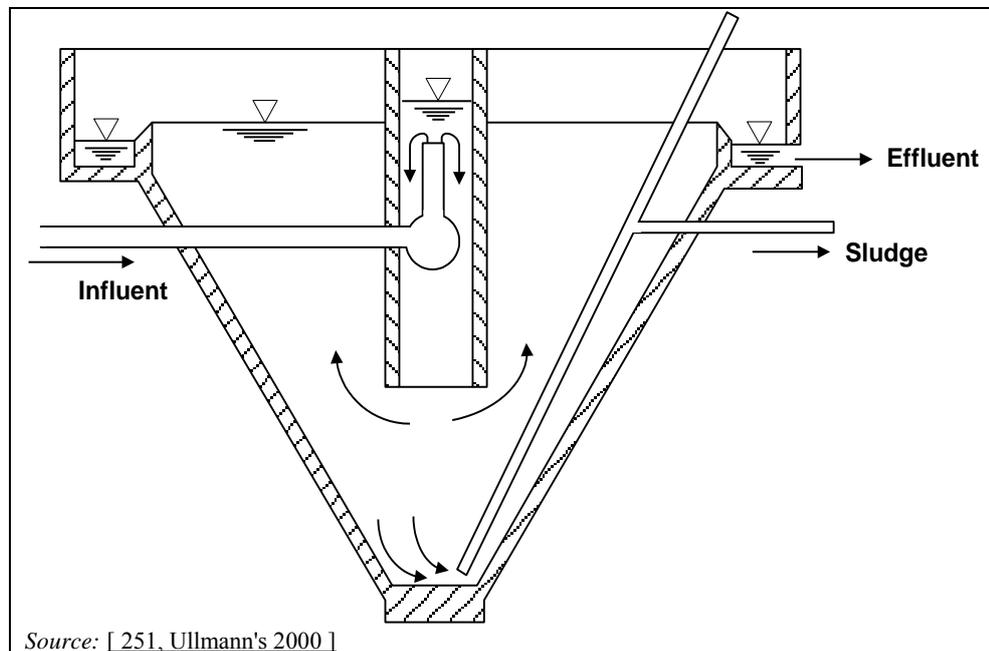
Figure 3.15: Hopper-bottom tank

- lamina or tube settlers, where plates are used to enlarge the sedimentation surface (see Figure 3.16).

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

- the simultaneous dosing of coagulants via multiple injection points;
- a preference for plug flow systems, where applicable;
- a 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 the flocculant.

To ensure an 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.

Source: [31, Kemmer 1988]
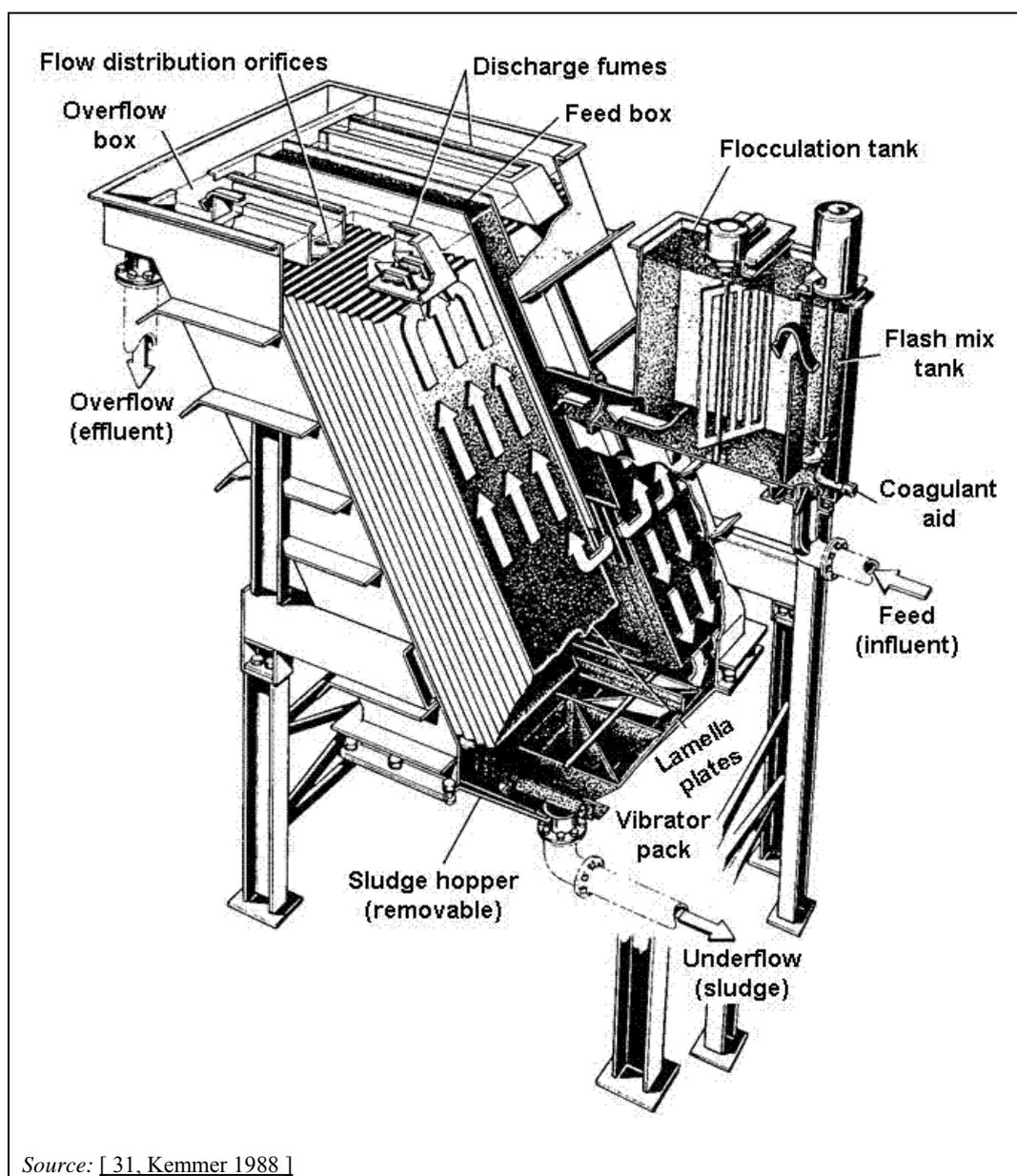
Figure 3.16: Lamina or tube settler

Achieved environmental benefits
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.

Abatement efficiencies and emission associated with the sedimentation of solids levels are given in Table 3.9.

Table 3.9: Abatement efficiencies and emission levels associated with the sedimentation of solids

Pollutant	Abatement efficiency (%)	Emission level (mg/l)	Comments
TSS	60–90 ([1])	5–35 ([2])	After final clarifier of WWTP
Settleable solids	90–95 ([1])	NI	─
Heavy metals	NI	NI	In particulate form, see Section 3.3.2.3.4.2
([1]) [247, COM 2003]. ([2]) As yearly average of 24-hour composite samples [222, CWW TWG 2013]. NB: NI = no information provided.			

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

Cross-media effects
Sedimented sludge and skimmed scum, if not suitable to recycle or reuse, 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, which 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 (see in particular Section 3.5.5.4). 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 and their amounts in terms of effects on the sedimentation of solids are given in Table 3.10.

Table 3.10: Cross-media effects associated with the sedimentation of solids

Consumable	Amount
Chemicals (coagulant/flocculant) ([1])	53–93 (kg/t oil, solid) ([2])
	0.5–100 (g/m^3 waste water) ([3])
Electric energy (kWh) ([4])	0.5–1.5
Nitrogen for inert atmosphere	NI
([1]) Organic polymer. ([2]) [36, NOREC 2000]. ([3]) [63, VITO 2010]. ([4]) For tank diameter of 25–35 m. NB: NI = no information provided.	

Operational data

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.

Applicability

Sedimentation is a separation technique widely used for many purposes and is 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 the addition of appropriate chemicals;
- separation of heavy metals or other dissolved compounds after precipitation (see Section 3.3.2.3.4.2), often with chemical support, followed at the end by filtration processes (see Sections 3.3.2.3.3.6 and 3.3.2.3.3.7);
- removal of activated sludge in a primary or secondary clarifier of a biological WWTP (see Section 3.3.3.1), often supported chemically.

Application limits and restrictions are given in Table 3.11.

Table 3.11:   Application limits and restrictions associated with the sedimentation of solids

Issue	Limit/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 VOCs
Solid concentration	No limits, provided the aqueous phase is still separable
pH (in the case of coagulation/floccu-lation)	Controlled pH range is essential during operation, otherwise performance of clarification is poor
Emulsions	Stable emulsions cannot be separated and broken by coagulation/flocculation; preceding emulsion breaking is required

Advantages and disadvantages are given in Table 3.12.

Table 3.12:   Advantages and disadvantages associated with the sedimentation of solids

Advantages	Disadvantages
•Simplicity of the installation, and thus not tending to fail •Removal efficiency can be increased by the 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

Economics

Economics associated with the sedimentation of solids are given in Table 3.13.

Table 3.13: **Economics associated with the sedimentation of solids**

Equipment	Investment costs (million)	Operating and maintenance costs
Sedimentation tank	EUR 1.2 ([1])	NI
	EUR 0.2–0.3/m³ ([2])	
	EUR 0.25 ([3])	
Lamina or tube settler	EUR 0.15 ([4])	Up to EUR 2.5 per m³ ([6])
	EUR 0.02 ([5])	

([1]) Per 1 000 m³ tank volume.
([2]) Cost per 1 000 m³ of concrete tank volume. Costs can be higher if the bottom of the sedimentation tank is slanted [63, VITO 2010].
([3]) Scraper blade of maximum 5 metre diameter [63, VITO 2010].
([4]) Capacity of 240 m³/h [63, VITO 2010].
([5]) Capacity of 20 m³/h [63, VITO 2010].
([6]) The use of a flocculation process can induce a rise in the costs as flocculating agents need to be bought. In this case the cost would vary according the matrix contents [216, Viavattene et al. 2010].

NB: NI = no information provided.

Investment costs are closely related to the size (surface) of the unit used to treat the waste water volume. An economy of scale effect is evident. Large tanks cannot easily be constructed in dense urban areas and the cost of land could affect the total cost [216, Viavattene et al. 2010].

Driving force for implementation
The driving force for implementation is to protect the downstream treatment facilities when it is used upstream of a treatment plant, and to comply with legal discharge standards by the removal of suspended solids and associated organics when it is used as a final treatment.

Example plants
Many plants in Europe use sedimentation of solids [222, CWW TWG 2013].

Reference literature
[1, Metcalf and Eddy 1991] [3, Environment Agency (England and Wales) 1997] [31, Kemmer 1988] [36, NOREC 2000] [63, VITO 2010] [216, Viavattene et al. 2010] [222, CWW TWG 2013] [247, COM 2003] [251, Ullmann's 2000]

3.3.2.3.3.5   Flotation

Description
Flotation is a process where solid or liquid particles or particulates are separated from the waste water phase by attaching to fine gas bubbles, usually air (nitrogen or fuel gas are commonly used in the oil industry). The buoyant particles accumulate at the water surface and are collected with skimmers [1, Metcalf and Eddy 1991].

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 gas bubbles.

There are three methods of flotation, distinguished by the way the gas (usually air) is added:

- vacuum flotation, where gas is dissolved at atmospheric pressure, followed by a pressure drop to allow the formation of bubbles;
- induced gas flotation (IGF)/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 gas flotation (DGF)/dissolved air flotation (DAF), where pressurised gas (e.g. air at 0.4–0.8 MPa, or 1.0–1.2 MPa for aluminium compounds) is dissolved into the waste water, or part of the total waste water, and subsequently released to form small bubbles.

A typical DAF device is presented in Figure 3.17.

Depending on the waste water content, it might be necessary to cover the flotation basin and to take the exhaust air to a gas abatement device. Facilities are necessary to store the flocculant/coagulant chemicals and the skimmed material.

Source: [1, Metcalf and Eddy 1991]
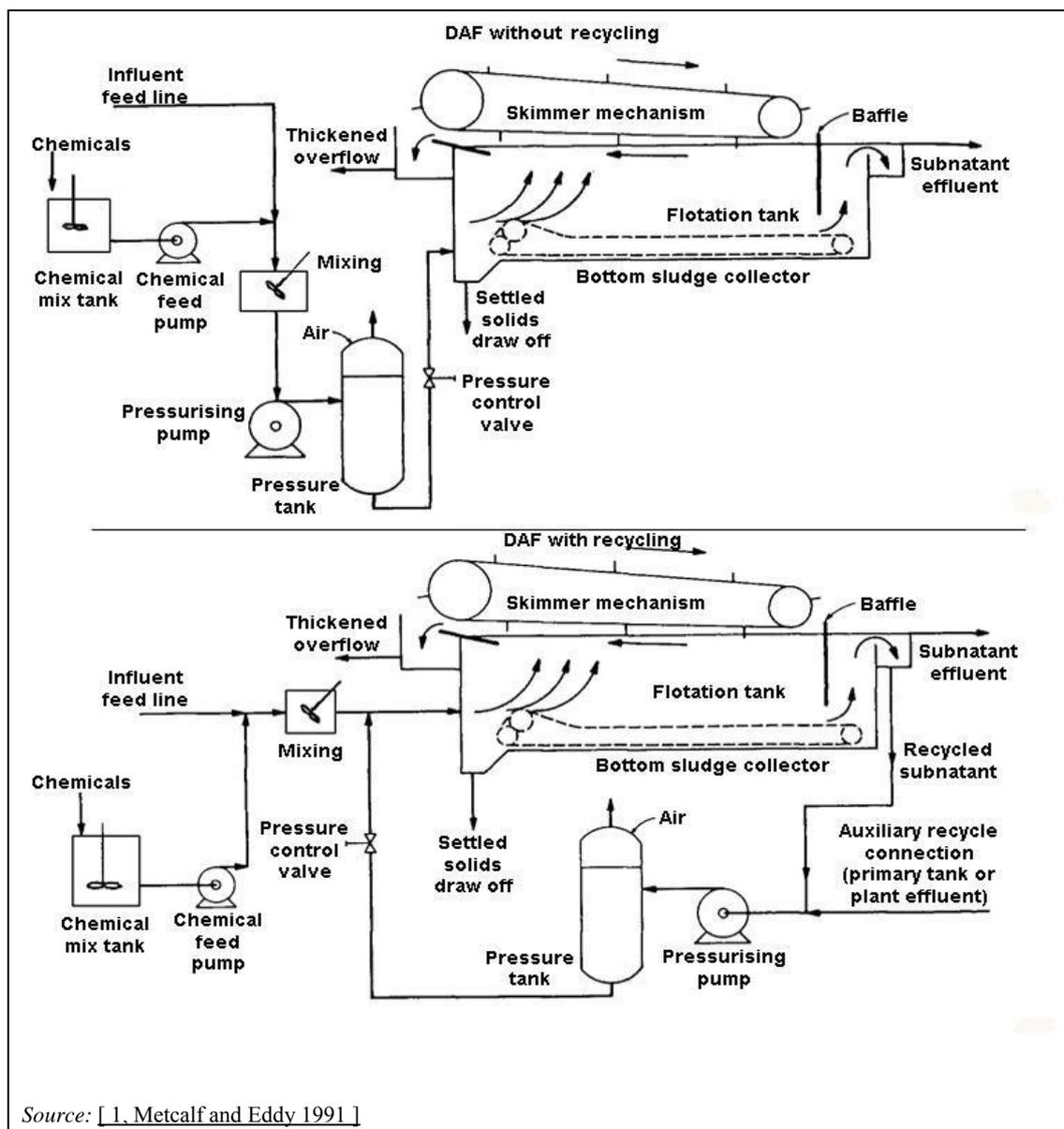
Figure 3.17: Dissolved air flotation with and without recycling

Achieved environmental benefits
Flotation is used to remove suspended solids, oil and fats and COD. Organic compounds are removed to the extent that they are present as solids or a suspension of droplets.

Abatement efficiencies and emission levels associated with flotation are given in Table 3.14.

Table 3.14:   Abatement efficiencies and emission levels associated with flotation

Pollutant	Abatement efficiency (%)	Emission level (mg/l)	Comments
TSS	90–98		See Figure 3.18
	85–96 ([1])	5–30 ([2])	—
Oil (both for IGF/IAF and DGF/DAF)	NI	5–15 ([3])	Depending on the effectiveness of the chemical(s) used to support flotation as well as the feed concentration of oil
	NI	2–10 ([4])	Chemical production, after several API separators

([1]) [96, Neumann et al. 1999].
([2]) As yearly average of 24-hour composite samples [222, CWW TWG 2013].
([3]) [227, CWW TWG 2009].
([4]) [33, ETBPP 1997].
NB: NI = no information provided.

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 vary depending on the respective applications of flotation.

Consumables and treatment amounts are given in Table 3.15.

Table 3.15:   Cross-media effects associated with flotation

Consumable		DAF treatment of activated sludge
Compressed air ([1])		0.53–0.55
Flocculant dose	mg/l ([2])	0.6–1.2
	kg/t ([3])	2.4–4.7
Energy (kWh/1 000 m³)		20.6

([1]) Relative to pressurised water (m³/m³).
([2]) Flocculant concentration in the waste water.
([3]) Amount of flocculant relative to the mass of suspended solids in the waste water.
Source: [96, Neumann et al. 1999]

Sources of noise are the pumps, the 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 (see Section 3.5.5.4). Retrofitting existing DAF units with covers is very difficult if they were not intended to be covered. For reducing emissions, in many cases a DAF unit replacement is required.

Operational data
Monitoring
To ensure reliable operation in terms of monitoring, the turbidity or parameters such as the COD/TOC (if low hydrocarbon contamination in the effluent) of the effluent has to be monitored for disturbances. Any excessive foam arising has to be detected in a timely manner (some foaming is desirable for effective separation). Effluent detection of COD/TOC and TSS is obligatory.

Applicability

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

- the particulates have poor settling characteristics (in the case of a poor sludge volume 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 of where and when flotation is applied include:

- at petrochemical sites as a subsequent treatment downstream of oil separation and prior to a biological WWTP;
- the removal of dyes and pigments from respective production waste water;
- recovering product or raw material, e.g. toluene from toluene/water emulsions [251, Ullmann's 2000], silver halides from the production of photographic chemicals, butylthion or polysilan from waste water streams;
- the separation of heavy metals from waste water;
- the separation of activated sludge from biological waste water treatment, either after final clarification [10, Rosenwinkel et al. 1999] or replacing it;
- thickening of activated sludge from a biological WWTP.

Application limits and restrictions are given in Table 3.16.

Table 3.16: Application limits and restrictions associated with flotation

Issue	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 are given in Table 3.17.

Table 3.17: Advantages and disadvantages associated with flotation

Advantages	Disadvantages
- Less volume and thus lower investment costs required than with sedimentation - With respect to solid removal, abatement efficiency unaffected by changes of flow rate and thus superior to sedimentation, see Figure 3.18 - Material recovery possible - High separation efficiency, higher dry matter content than with sedimentation	- Clogging of valves is possible - High potential for odour release; a cover may be required in case of odour issues, unless alternatives are effective (e.g. odour adsorbent) - Higher operating costs than sedimentation

NB: Insolubles content: 90–450 mg/l; pressurised water addition for flotation: 20 %.

Source: [251, Ullmann's 2000]
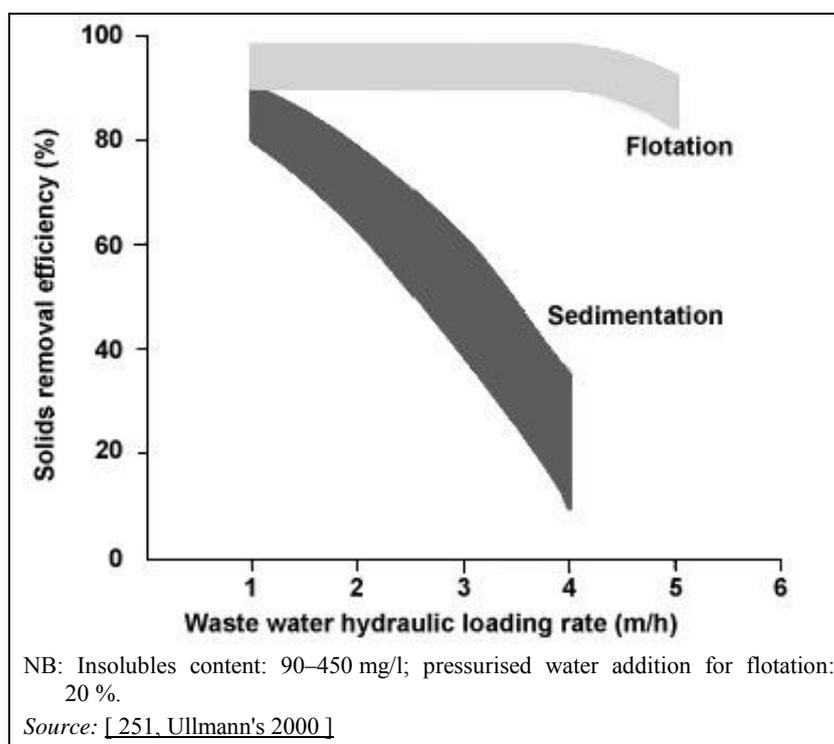
Figure 3.18: Comparison of separation efficiency of DAF versus sedimentation

Economics
The costs of a flotation unit vary widely, depending on the purpose (Table 3.18).

Table 3.18: Economics associated with air flotation

	Flow rate	Investment costs (million)	Annual operating costs (thousand)
DAF/activated sludge	1 200 m³/h	DEM 5.0 (EUR 2.5) (^{1})	DEM 800 (EUR 410) (^{2})
DAF/as decentralised final treatment (^{3})	50 m³/h	NI	DEM 4 500 (EUR 2 300) (^{4})
DAF System 3 (^{5})	30 m³/d	EUR 0.074	NI
DAF System 4 (^{6})	70 m³/h	EUR 0.11	

(^{1}) Investment costs include engineering design, civil engineering works, and site preparation. Flotation was put into operation in 1997 [96, Neumann et al. 1999]. Average currency conversion rate for 1997: EUR/DEM = 1.962.
(^{2}) Annual operating costs for 1998 [96, Neumann et al. 1999]. Average currency conversion rate for 1998: EUR/DEM = 1.972.
(^{3}) Total operating costs, including chemicals for neutralisation, precipitation and flocculation, dewatering of flotate, incineration of sludge [251, Ullmann's 2000].
(^{4}) Fixed currency conversion rate from January 1999 onwards: EUR/DEM = 1.956.
(^{5}) The investment costs of EUR 0.075 million (from the year 2008) include a DAF system with dose measurement device, equipment for measurement and regulation, slurry tank and control equipment [63, VITO 2010].
(^{6}) The investment costs of EUR 0.1 million (from the year 2007) include a DAF system with a flocculator, polyelectrolyte production unit, dosing unit and slurry pump [63, VITO 2010].
NB: NI = no information provided.

Indicative investment and operating costs for a DAF plant are given in Table 3.19 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.

Table 3.19: Investment and operating costs associated with air flotation

Flow rate (m³/h)	Investment costs (in million) ([1])	Annual operating costs (in thousand) ([1])
10	GBP 0.1 (EUR 0.12)	GBP 10 (EUR 12)
100	GBP 0.1 (EUR 0.12)	GBP 20–30 (EUR 24–37)
1 000	GBP 0.5 (EUR 0.61)	GBP 50–80 (EUR 61–98)
10 000	GBP 1.0 (EUR 1.2)	GBP 500–800 (EUR 610–980)
([1]) Average currency conversion rate for 1996: EUR/GBP = 0.8188.		
Source: [32, ETBPP 1996]		

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 investment costs, albeit at the expense of higher operating costs. A comparison may yield a space requirement for sedimentation 50 times greater than that of 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 [251, Ullmann's 2000].

Driving force for implementation
The main driving force for implementation is to remove suspended solids, oil and fats and organic pollutants from waste waters.

Example plants
Sectors where flotation is used include the chemical industry [222, CWW TWG 2013], the food industry, tank cleaning and refineries.

Reference literature
[1, Metcalf and Eddy 1991] [10, Rosenwinkel et al. 1999] [32, ETBPP 1996] [33, ETBPP 1997] [36, NOREC 2000] [63, VITO 2010] [96, Neumann et al. 1999] [222, CWW TWG 2013] [227, CWW TWG 2009] [251, Ullmann's 2000]

3.3.2.3.3.6   Filtration

Description
Filtration describes the separation of solids from waste water effluents passing through a porous medium. This technique is rarely used as a stand-alone treatment and is generally combined with the sedimentation of solids (see Section 3.3.2.3.3.4) or flotation (see Section 3.3.2.3.3.5). Filters typically require a cleaning operation, i.e. backwashing, with the reverse flow of fresh water and the accumulated material returned to the sedimentation tank (Section 3.3.2.3.3.4).

Commonly used types of filter systems include:

- **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 sewerage treatment and the removal of activated sludge flocs, its efficiency is 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 3.3.2.3.3.7);

- the **belt filter press**, which is largely used for sludge dewatering, but also for liquid/solid separation operations (see Section 3.4.2.2);
- **filter press**, which is usually used for sludge dewatering (see Section 3.4.2.2), 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-media. The operation can be semi-continuous (where filtration and backwashing occur sequentially) or continuous (where filtration and backwashing operate simultaneously). The main differences between the two operation modes are:

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

Sand filters work either by the force of gravity or an applied pressure force. Examples are given in Figure 3.19 for the conventional downflow multi-media gravity-flow sand filter and in Figure 3.20 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 rotary 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 of a rotary vacuum filter is given in Figure 3.21.

Belt filter presses and filter presses as typical sludge dewatering facilities are described in Section 3.4.2.2.

Filter media can be characterised in terms of criteria, such as [253, Ullmann's 2009]:

- cut size, i.e. the particle size that can pass through the filter medium;
- permeability; high permeability is characterised by a 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.
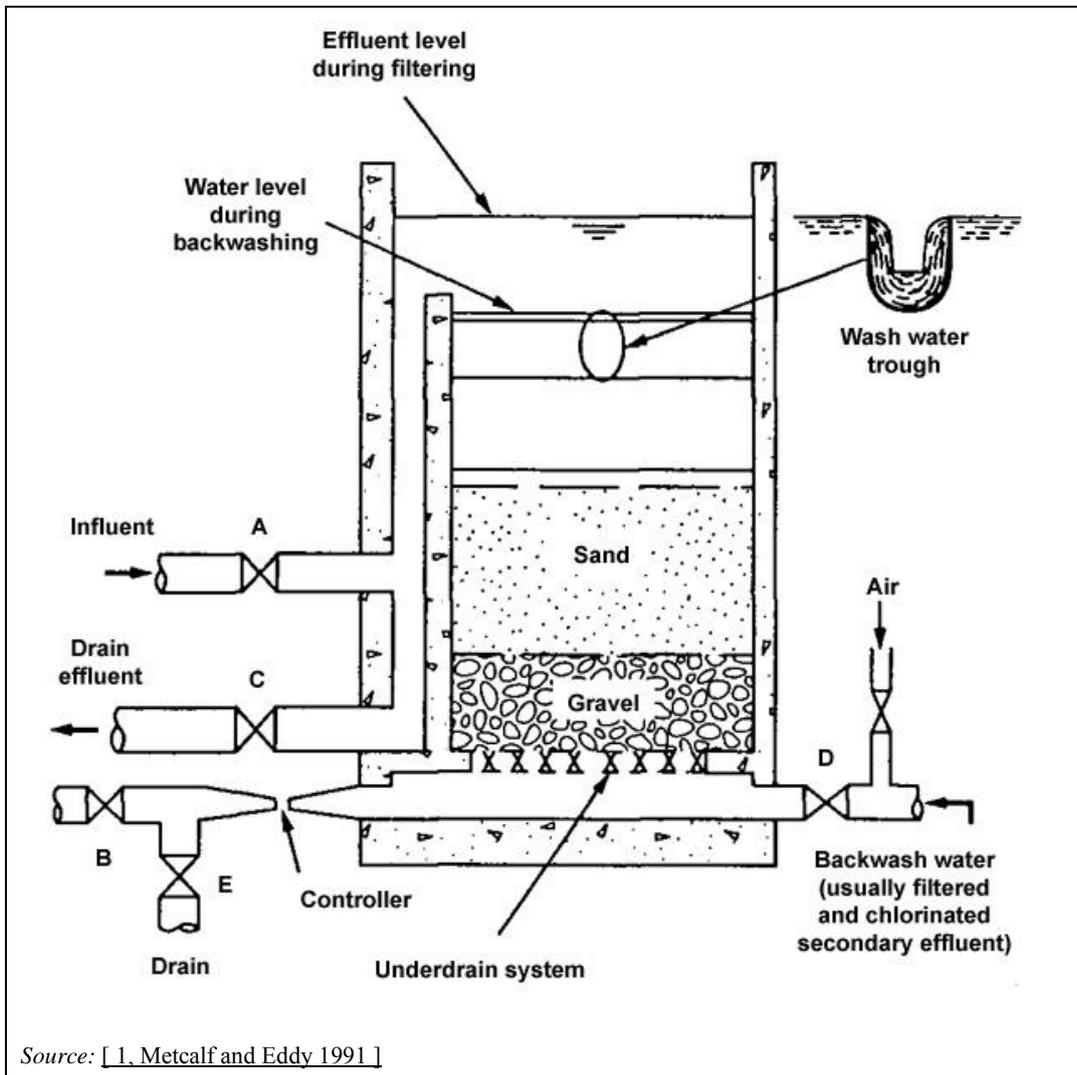
Source: [1, Metcalf and Eddy 1991]

Figure 3.19: Conventional multi-media gravity-flow sand filter
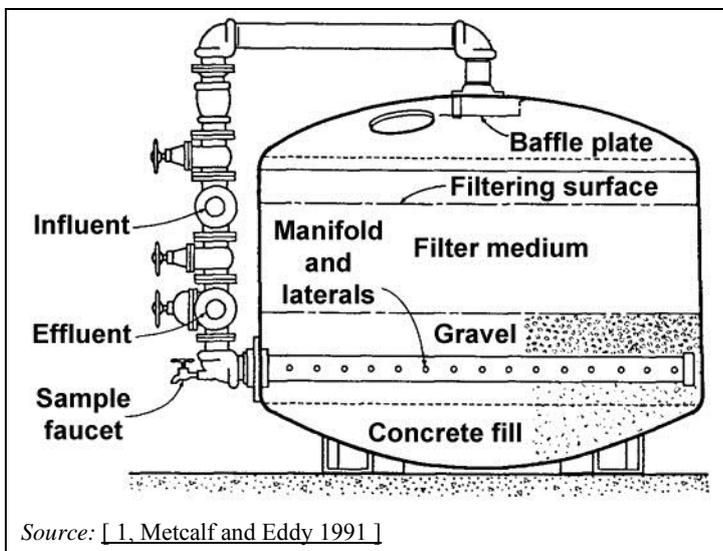
Source: [1, Metcalf and Eddy 1991]

Figure 3.20: Pressure filter

a) Dewatering zone, b) Rotary valve,
c) Settling zone, d) Suction zone

Source: [253, Ullmann's 2009]
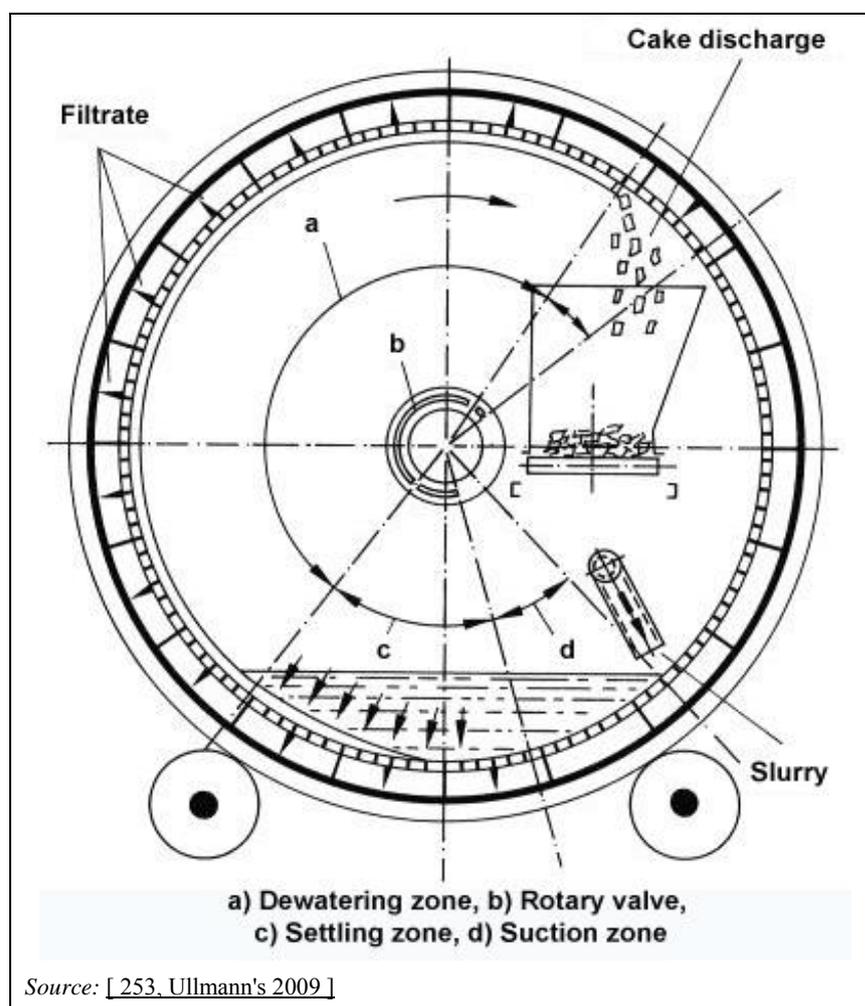
Figure 3.21: Rotary vacuum filter

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 that is permeable for 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 diatomaceous earth perlites, Fuller's earth powdered glass, coal preparations, cellulose fibres, wood pulp, paper stock, bagasse, talc and plastics [253, Ullmann's 2009].

Filter aids are used in precoating, 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.

Achieved environmental benefits
The environmental benefits that can be achieved by using filtration are given in Table 3.20.

Table 3.20: Abatement efficiencies and emission levels associated with filtration

Pollutant	Abatement efficiency (%)	Emission level (mg/l)	Comments
TSS	NI	< 10 mg/l ([1])	Activated sludge floc
	50–99.99 ([2])	NI	Sand filter, dependent on filter aids
([1]) [247, COM 2003]. ([2]) [63, VITO 2010]. NB: NI = no information provided.			

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 to 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 (see examples above in this chapter) [253, Ullmann's 2009].

Table 3.21 lists consumables for the filtration technique.

Table 3.21: Consumables associated with filtration

Consumable	Sand filter	Drum filter
Water for backwashing	In oily water removal, the backwash water is typically 4–7 % of the forward processed flow volume	NI
Water for vacuum generation	NI	NI
Filter aids	NI	NI
Energy (kWh/1 000 m^3)	NI	NI
Pressure drop	NI	NI
NB: NI = no information provided.		

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

If odorous substances are released, closed devices might be necessary (see Section 3.5.5.4). Pressure filters and filter presses are placed in closed vessels and the exhaust air passes through a duct to a gas abatement system.

Operational data
Monitoring
To ensure reliable operation, the turbidity of the filtered effluent has to be monitored to recognise disturbances, or a breakthrough with the semi-continuous sand filter. The pressure drop has to be registered to indicate clogging and barring.

Applicability
In waste water treatment, filtration is frequently used as the final separation stage after sedimentation processes (see Section 3.3.2.3.3.4) or flotation (see Section 3.3.2.3.3.5), if low emissions of particulates are wanted, such as:

- separation of floc, heavy metal hydroxides, etc. after sedimentation, to cope with discharge requirements;
- removal of activated sludge after the central biological 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 are given in Table 3.22.

Table 3.22:   Application limits and restrictions associated with filtration

Issue	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 are given in Table 3.23.

Table 3.23:   Advantages and disadvantages associated with filtration

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 sand filters • Breakthrough can cause additional pollution of the effluent

Economics
Filtration is a relatively inexpensive simple treatment option usually used to complement other more complex process. The investment costs are related to the volume of water to be treated. Investment and operating costs for a simple filtration system are given in Table 3.24.

Table 3.24:   Economics associated with filtration

Filtration system	Investment costs	Operating and maintenance costs
Simple filtration system (^{1})	EUR < 0.1 per m^3	About EUR 0.01 per m^3
Industrial continuous sand filtration system (^{2})	EUR 50 000	NI

(^{1}) [216, Viavattene et al. 2010].
(^{2}) Flow rate 50 m^3/h [63, VITO 2010].
NB: NI = no information provided.

Driving force for implementation
The driving force for implementation is to reduce the amount of suspended solids in the final waste water effluents and to meet the legal discharge standards. If filtration is used for sludge treatment purposes, the driving force for implementation is to reduce the water content and subsequent volume of the sludge produced.

Example plants
Sectors where sand filtration is used include the chemical industry, refineries, car washes, the food and drink industry, slaughterhouses, and the surface treatment of metals.

Reference literature
[1, Metcalf and Eddy 1991] [63, VITO 2010] [216, Viavattene et al. 2010] [247, COM 2003] [253, Ullmann's 2009]

3.3.2.3.3.7   Microfiltration and ultrafiltration

Description
Microfiltration (MF) and ultrafiltration (UF) are membrane processes that retain certain substances contained in waste waters on one side of the membrane. The liquid that permeates through the membrane is referred to as the permeate. The liquid that is retained is referred to as the concentrate. 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 Section 3.3.2.3.3.6.

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

Typical characteristics are shown in Table 3.25.

Table 3.25:   Characteristics of microfiltration (MF) and ultrafiltration (UF)

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 1 000–100 000 g/mol for solutions
Permeate flow ($l/(m^2 \times h)$)	50–1 000	< 100
Cross-flow speed (m/s) ([2])	2–6	1–6
Membrane type ([3])	Polymeric, or ceramic asymmetric	Polymeric, or ceramic asymmetric
Membrane configuration ([3])	Hollow-fibre, tubular	Hollow-fibre, tubular
([1]) [3, Environment Agency (England and Wales) 1997]. ([2]) [254, Ullmann's 2009]. ([3]) [33, ETBPP 1997].		

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 include glass fibre, polycarbonate, polyvinylidene fluoride, cellulose acetate and 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.

Polyvinylidene fluoride 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.

Achieved environmental benefits
The TSS abatement efficiency associated with microfiltration and ultrafiltration is generally
> 99 % [63, VITO 2010].

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 reused or recycled in the industrial process,
thus reducing water input and discharge.

Consumables are given in Table 3.26.

Table 3.26:   Consumables associated with microfiltration and ultrafiltration

Consumables	MF	UF
Membrane material	NI	NI
Chemicals (anti-scaling, anti-fouling, backwashing, etc.)	NI	NI
Energy (kWh/m^3)	2–20 ([1])	1–10 ([1])
Pressure drop	See Table 3.25	See Table 3.25
([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 [88, Mulder 1994].		
NB: NI = no information provided.		

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.

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

Applicability
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
insoluble heavy metals, is desired. The choice between MF and UF depends on the particle size.

Common MF applications include [33, ETBPP 1997] [10, Rosenwinkel et al. 1999]

- degreasing processes;
- metal particle recovery;
- metal plating waste water treatment;
- sludge separation after the 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 compounds, e.g. dyes and paints, with molecular weights greater than 1 000;
- segregation of oil/water emulsions;
- separation of heavy metals after complexation or precipitation;
- separation of compounds not readily degradable in sewerage treatment effluents, which are subsequently recycled to the biological stage;
- pretreatment step prior to reverse osmosis (see Section 3.3.2.3.4.7) or ion exchange (see Section 3.3.2.3.4.11).

Application limits and restrictions are given in Table 3.27.

Table 3.27:   Application limits and restrictions associated with microfiltration and ultrafiltration

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

Advantages and disadvantages are given in Table 3.28.

Table 3.28:   Advantages and disadvantages associated with microfiltration and ultrafiltration

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

Economics
Economics associated with microfiltration and ultrafiltration are given in Table 3.29.

Table 3.29:   Economics associated with microfiltration and ultrafiltration

Technique	Flow rate	Investment costs	Operating costs	Replacement costs
MF	NI	GBP 400–1 500 (EUR 570–2 150) per m^2 membrane (^{1})	NI	GBP 80–350 (EUR 110–500) per m^2 membrane (^{1})
	25 m^3/d (^{2})	EUR 25 000–50 000 (^{2})	EUR 0.10–0.15 per m^3 permeate produced (^{2})	NI
UF	NI	GBP 400–1 500 (EUR 570–2 150) per m^2 membrane (^{1})	NI	GBP 80–350 (EUR 110–500) per m^2 membrane (^{1})
	650 m^3/h (^{2})	About EUR 2 000 000 (^{2})	NI	NI
	64 m^3/d (^{2})	About EUR 56 000 (^{2})	NI	NI

(^{1}) For hollow fibre, spiral and ceramic membranes [33, ETBPP 1997]. Average currency conversion rate for 1997: EUR/GBP = 0.6971.
(^{2}) [63, VITO 2010].
NB: NI = no information provided.

The total investment costs, including automated cleaning facilities, can be broken down approximately as follows [33, ETBPP 1997]:

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

The operating costs [33, ETBPP 1997] are 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 requirements.

The operating costs can be broken down approximately as follows [33, ETBPP 1997]:

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

Driving force for implementation
The driving force for using the technique is to achieve a quasi-solid-free effluent for further use or discharge.

Example plants
Sectors where microfiltration or ultrafiltration are used include the food industry (cheese, milk, juices, wine, beer), the metal industry, the textile industry, and the pharmaceutical industry.

Reference literature
[3, Environment Agency (England and Wales) 1997] [10, Rosenwinkel et al. 1999] [33, ETBPP 1997] [63, VITO 2010] [88, Mulder 1994] [254, Ullmann's 2009]

3.3.2.3.3.8   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 the subsequent separation of de-emulsified oil by coagulation/flocculation and flotation (see Section 3.3.2.3.3.5).

The commonly used oil-water separators are:

- the **American Petroleum Institute (API) separator** 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 3.22);

- 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 3.23);

- the **corrugated plate interceptor (CPI)**, equipped with corrugated plate packs placed countercurrent and an oil skimming device, not suitable to intercept large slugs, but possessing a good separation efficiency (see Figure 3.24).

Source: [31, Kemmer 1988]
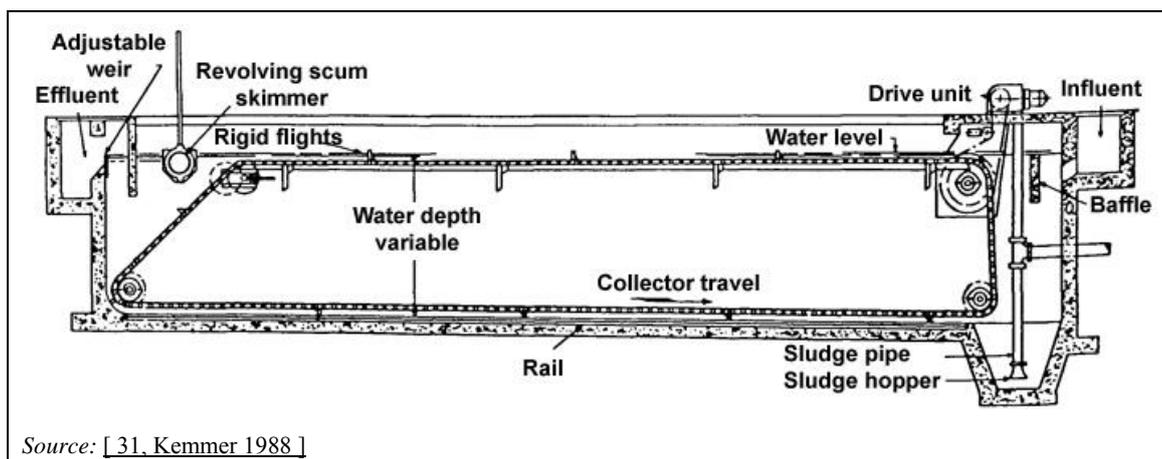
Figure 3.22: American Petroleum Institute (API) separator

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.
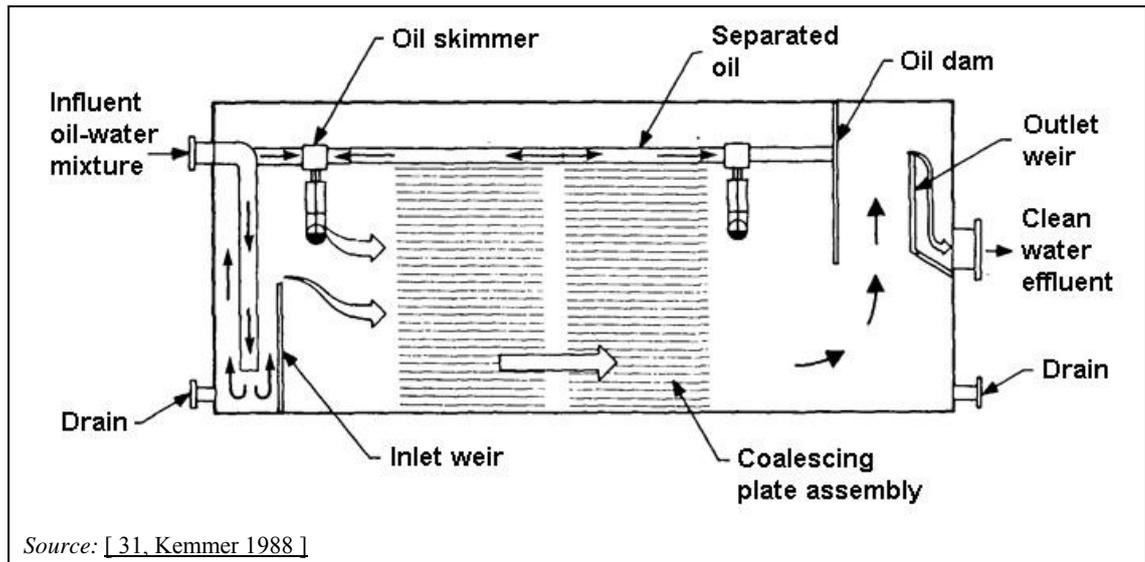
Figure 3.23: Parallel plate interceptor (PPI)
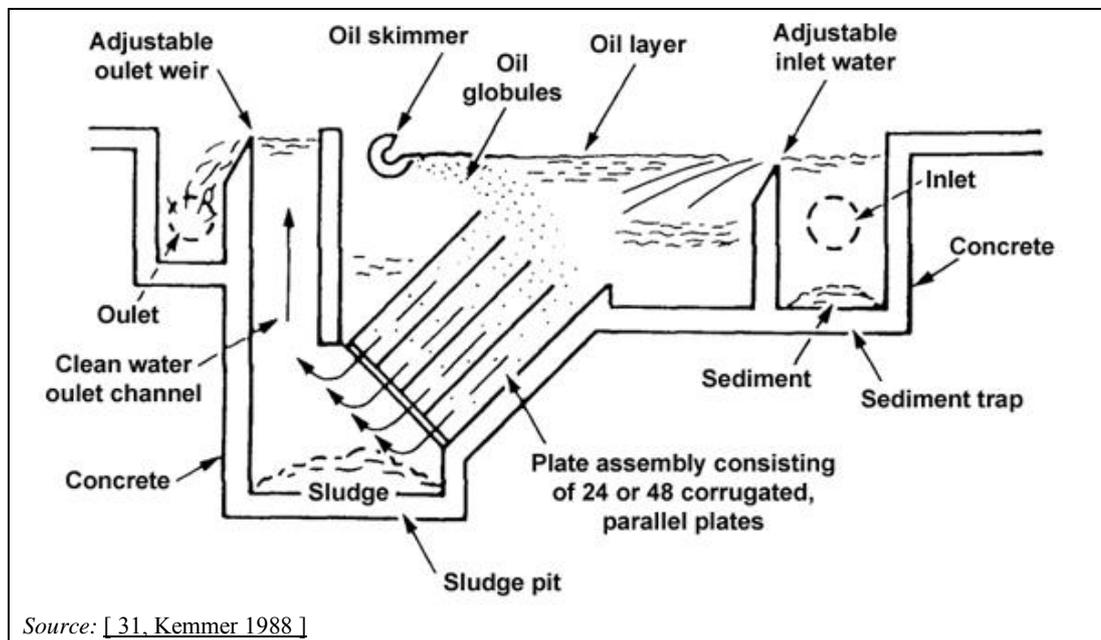
Figure 3.24: Corrugated plate interceptor (CPI)

Achieved environmental benefits
Abatement efficiencies and emission levels associated with oil-water separation are given in Table 3.30.

Table 3.30:   Abatement efficiencies and emission levels associated with oil-water separation

Pollutants	Abatement efficiency ([1]) (%)	Emission level ([1]) (mg/l)	Comments
Oil	80 ([2])–95	NI	—
	NI	40–70 mg/l ([3])	API separator, chemical industry
Solid	90–95	NI	—
([1]) The abatement efficiencies and emission levels are indicative and depend on the specific type and design of oil-water separators used, the feed concentration of pollutant(s), the physical characteristics of the oil-water mixtures present in the waste water (i.e. size of the oil droplets), etc. When the oil exists as extremely small particles and emulsions (e.g. when surfactants, solvents or detergents are present), oil-water separators may not be very effective [233, Oldcastle 1996].			
([2]) [227, CWW TWG 2009].			
([3]) [33, ETBPP 1997].			
NB: NI = no information provided.			

Cross-media effects
The skimmed oil is generally sent back to the process units, where it is reused 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 often major contributors to VOC releases in waste water treatment systems of which they are part. Surface covering achieves a significant VOC release reduction. 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. Surface covering achieves a VOC release reduction of about 95 % and should be considered when emissions from the WWTP are a significant contributor to the total VOC emissions of the plant.

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

Consumables are given in Table 3.31.

Table 3.31:   Consumables associated with oil-water separation

Consumables	API	PPI	CPI
Nitrogen from pressurised system as a safety device ([1])	0.05 m/h	NI	NI
Energy (kWh/m^3)	NI	NI	NI
([1]) Nitrogen gas flow relative to surface area (m^3/(m^2×h)).			
NB: NI = no information provided.			

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

Applicability
Oil-water separation is applied to remove oil, grease and other non-soluble liquids lighter than the aqueous phase from waste water, mainly at petrochemical sites. It is normally not a stand-alone process, but followed by flotation (IAF or DAF), supported by coagulation/flocculation (see Section 3.3.2.3.3.5). The API separator is also used as a control device to protect

downstream equipment against large oil slugs originating, e.g. from an operational failure, whereas the PPI and CPI show a higher efficiency in the removal of smaller oil droplets.

Advantages and disadvantages are given in Table 3.32.

Table 3.32: Advantages and disadvantages associated with oil-water separation

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

Economics
Economics associated with oil-water separation are given in Table 3.33.

Table 3.33: Economics associated with oil-water separation

Oil-water separator	Flow rate	Investment costs	Operating costs
API	NI	NI	NI
PPI	NI	NI	NI
CPI	2 l/s	EUR 3 000–3 500	NI
	10 l/s	EUR 5 500–8 500	NI
NB: NI = no information provided.			
Source: [63, VITO 2010]			

For effective emulsion breaking, large quantities of support products are often needed which makes the technique relatively expensive. The costs associated with breaking emulsions are mainly determined by the required quantity of chemicals and the price of these chemicals (the dosage level and the cost per kilogram). Dosage is determined by the quantity of emulsified matter and normally lies between 0.5 g/m^3 and 1 000 g/m^3.

Driving force for implementation
The drivers for using the technique is oil recovery for reuse/recycling and pollution prevention.

Example plants
Oil-water separation is used at almost all petrochemical installations (e.g. WWTP #26 [222, CWW TWG 2013]) as well as in refineries.

Reference literature
[31, Kemmer 1988] [33, ETBPP 1997] [63, VITO 2010] [222, CWW TWG 2013] [227, CWW TWG 2009] [233, Oldcastle 1996]

3.3.2.3.3.9   Hydrocyclone

Description
A hydrocyclone is used to separate suspended solids with a diameter of 5 μm to 1 000 μm that are likely to sink and resistant to shearing forces. It separates the particles by using the centrifugal force generated as the liquid enters the cyclone tangentially at high speeds and is accelerated by the conical middle section. This creates a liquid vortex in the cyclone. A hydrocyclone is often divided into four parts:

1. Inlet section: consists of a cylindrical supply chamber into which the incoming flow enters.
2. Overflow section: light particles leave through this section at the top of the hydrocyclone.
3. Conical section: consists of a cone-shaped surface where the liquid accelerates. This acceleration is caused by the angle and the geometrics of the conical surface which helps in achieving higher centrifugal forces.
4. Tail section: located at the bottom of the hydrocyclone for extending the retention period for separation.

The smaller the diameter of the cyclone, the greater the centrifugal force that will be generated as the liquid is forced to take a sharp turn. Light components leave the hydrocyclone through the top, while heavier components are collected at the bottom. The presence of centrifugal forces both in hydrocyclones and in centrifuges might be confusing; however, they are two different pieces of equipment. A hydrocyclone does not have moving parts and the magnitude of the centrifugal force generated is around 1 000 times greater than gravity, whereas a centrifuge is an equipment with moving parts generating a centrifugal force greater than that in a hydrocyclone. If a solid particle settles by gravity within two minutes then a hydrocyclone is likely to be selected for the particle separation purpose. On the other hand, if the settling of the particle takes more than two minutes, then a centrifuge is likely to be selected.

The separation capability when various hydrocyclones are compared is expressed as 'd_{50} cut-size'. The 'd_{50} cut-size' represents the minimum size of the particles that are at least 50 % removed by the cyclone. These particles are then separated as slurry at the bottom of the cyclone. The dry matter content in the slurry is between 1 % and 10 %. A hydrocyclone designed for a flow of 100 m^3/h takes up around 20 m^2.

Achieved environmental benefits
The removal of suspended solids with a diameter of 5 μm to 1 000 μm and likely to settle within two minutes under gravitational force is an environmental benefit of this technique.

Cross-media effects
Depending on the application, a layer of sludge will form at the bottom of the hydrocyclone, which must be disposed of or subsequently processed.

Operational data
For crude oil processing, cyclones are used to separate oil and water and oil droplets equal to or greater than 30 μm with a removal efficiency of 98 %.

Applicability
A hydrocyclone should ideally feature a consistent supply of feed. The presence of long fibres in the liquid should be avoided when hydrocyclones are used. Hydrocyclones have a wide range of applications and are primarily used as a separation technique for the:

- separation of fine particles: the removal of large crystals in crystallisation systems;
- removal of large particles: such as the removal of waste from fruit juices;
- preparation of solutions or suspensions via controlled mixing of solid particles and water;
- gravitational separation of organic material from sugar beet effluents;
- separation of oil and water.

Economics
For a steel hydrocyclone system with standard instrumentation and for oil separation from an aqueous flow of 1 000 m^3/d, the investment costs amount to approximately EUR 250 000. These costs only relate to the investment costs concerning the hydrocyclone installation. They include the required equipment like pumps, piping and sludge tanks. Other costs, like water pretreatment, drainage, drying, electrical and mechanical installation costs, have not been included.

Driving force for implementation
To remove suspended solids with a diameter of 5 μm to 1 000 μm which are likely to settle under gravitational force is the driving force for the implementation of hydrocyclone.

Example plants
Levis Akzo Nobel BE – Vilvoorde plant (production of varnish).

Reference literature
[63, VITO 2010]

3.3.2.3.3.10   Electrocoagulation

Description
The aim of electrocoagulation is to form precipitates and compounds between colloids so these substances can be separated in subsequent operations. The release of coagulants in the waste water to be treated is realised by electrolytically dissolving an electrode (i.e. anode, normally made of Fe or Al). When the electrode is dissolved, gas is released (i.e. O_2, H_2) which results in a flotation effect. If necessary, a (support) flocculant can be added to improve the flotation yield.

A schematic of the technique is presented in Figure 3.25.
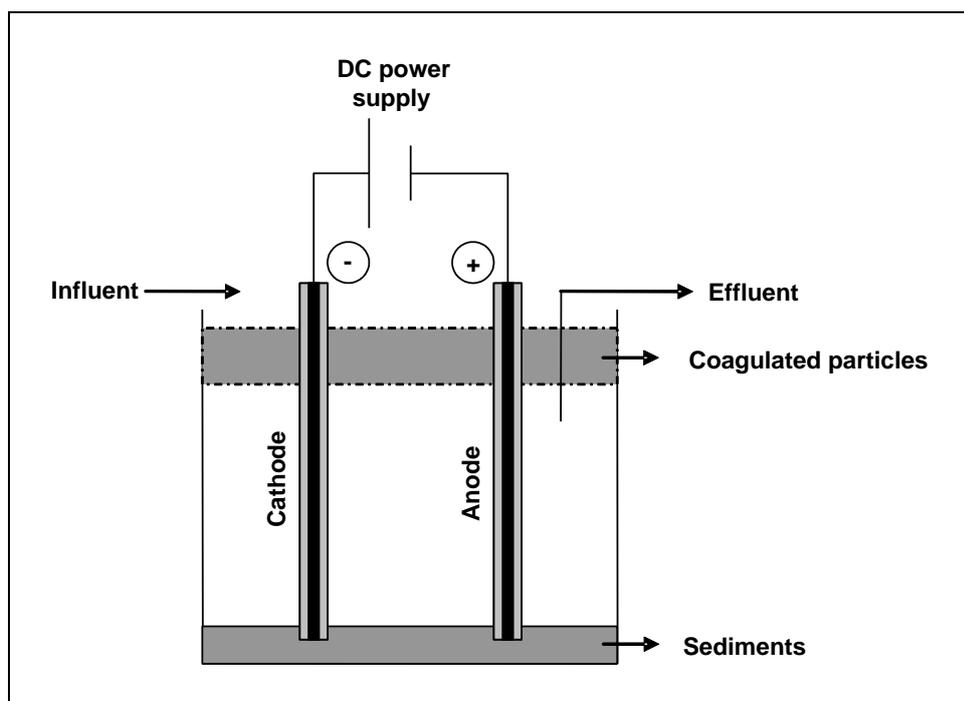
Figure 3.25: Electrocoagulation

In its simplest form, an electrocoagulation reactor consists of an electrolytic cell with an anode and a cathode. When the electrodes are connected to a power supply, an oxidation reaction takes place at the anode (positive electrode), while a reduction reaction takes place at the cathode (negative electrode).

Electroflotation could possibly be implemented after electrocoagulation. During electroflotation, electrolysis is used to split H_2O into H_2 and O_2. This involves the creation of gas bubbles, which ensure flotation. This approach is suited to small-scale systems, and when electricity is inexpensive.

Achieved environmental benefits
Electrocoagulation can be implemented for the removal of:

- settleable, suspended and dissolved substances;
- suspended substances and colloidal particles by destabilising surface loads;
- animal and plant oils and fats;
- organic compounds (BOD and COD);
- nutrients (e.g. phosphates);
- heavy metals in the form of oxides or insoluble Fe or Al precipitates (e.g. As, Cd, Co, Cr(VI), Cu, Hg, Mo, Ni, Pb and Zn);
- inorganic salts (e.g. CN^-);
- complex organic molecules, e.g. colourants (oxidation).

Furthermore, electrocoagulation can be implemented for breaking down oil emulsions in water, and the inactivation of bacteria, viruses and cysts.

Although a certain drop in dissolved COD is observed in many cases, this technique is not particularly suited for the removal of dissolved organic molecules, though it is suited for the removal of heavy metals, emulsions and colloids. Removal yields for metals, emulsions and colloids are comparable to those of a classic physico-chemical treatment (using coagulation and flocculation, see Section 3.3.2.3.3.3).

Cross-media effects
The silt is more compact and easier to dewater than in conventional physico-chemical treatment (using coagulants and flocculants, see Section 3.3.2.3.3.3).

In principle, no support substances are added unless the conductivity of the waste water has to be increased (by the addition of salts). Active substances (coagulants in the form of Fe or Al) are released via anodic reactions and react with the pollutants present in the waste water. The anode therefore needs to be replaced on a regular basis due to its gradual dissolution in the waste water.

Energy consumption is another cross-media effect.

Operational data
Minimum conductivity of waste water is required, which is achieved by the addition of salts.

Although the technique itself is very simple, potential reactions could be complex and difficult to predict. In general, the more difficult the waste water matrix (the amount and type of pollutants present), the more complex the reactions and the more unpredictable the result. Laboratory tests are needed to verify the applicability of the technique.

Applicability
Advantages and disadvantages are given in Table 3.34.

Table 3.34:   Advantages and disadvantages associated with electrocoagulation

Advantages	Disadvantages
• Relatively easy installation and operation • The formed silt floccules are larger, more stable and easier to dewater than classic physico-chemical silt • In comparison with physico-chemistry, the effluent of electrocoagulation contains fewer dissolved organic substances • It is possible to remove very small colloidal particles • The gas bubbles formed will push the light silt upwards, where it can be easily removed • The technique contains no or very few moving parts and is operated electronically, whereby maintenance costs (other than cleaning and replacing electrodes) are fairly low • No chemicals are needed; coagulant is released by anode reactions. As a result, chemical overdose is not possible	• The anode is dissolved in a waste water flow because of the oxidation, and must thus be replaced on a regular basis • The cathode is subjected to passive reactions (precipitation from reduced metals and hydroxides) that, as time passes, increase the resistance of the cell and thus reduce the yield • Depending on the conductivity and pollutants, the electrical capacity required in the cell could rise significantly

Economics
Average costs are equal to or higher than conventional techniques (e.g. coagulation and flocculation, see Section 3.3.2.3.3.3). For the treatment of waste water with electrocoagulation, a minimum of EUR 0.15 per m^3 can be anticipated for large installations. These costs arise primarily from the use of electricity and, to a lesser degree, from the replacement of electrodes.

To treat a waste water flow of 1 m^3/h with a load of ± 200 mg metals/l, investment costs of about EUR 150 000 can be foreseen. In this case, energy use amounts to 1 kW/m^3.

To treat a waste water flow of 4 m^3/d with a load of 1 500 ppm of TP, an investment of about EUR 100 000 can be anticipated (without silt treatment and disposal). The removal yield for TP amounts to 80 %. The total treatment cost amounts to EUR 15 per m^3 of waste water treated.

A company that coats metal surfaces with chromium has a waste water volume of 250 m^3/yr. The energy used by the company to run the technique is in the range of 0.8–1 kW/m^3 of waste water treated, and the total treatment cost amounts to EUR 19 per m^3 of waste water treated. Concentrations of heavy metals in the effluent after treatment are less than 0.2 ppm, thus the water can be reused.

Driving force for implementation
The driving force for implementing the technique is to reduce the discharge of pollutants to the receiving water.

Example plants
Sectors in which electrocoagulation is used include paint, gloss, varnish and printing-ink production, as well as the surface treatment of metals.

Reference literature
[63, VITO 2010]

3.3.2.3.4 Soluble non-biodegradable or inhibitory contaminants/physico-chemical treatment

3.3.2.3.4.1 Overview

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 a source for refractory TOC;
- inhibitory organic or inorganic compounds that disturb the biological process in a biological WWTP, for example solid materials and sand, emulsions, oil and fat.

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 3.3.2.3.3 (see Section 3.3.2.3.4.2 and 3.3.2.3.4.3);
- chemical degradation processes to form biodegradable contaminants (see Sections 3.3.2.3.4.4 to 3.3.2.3.4.6);
- physical elimination processes (see Sections 3.3.2.3.4.10 to 3.3.2.3.4.17);
- incineration processes to form gaseous and solid residues that can be separated from the waste water stream (see Section 3.3.2.3.4.18).

On new chemical sites in Germany it is common practice to use these pretreatment operations (or process-integrated techniques instead) with tributary streams carrying a relevant non-biodegradable load (e.g. TOC elimination rates below 80 % and a refractory TOC load of about 20 kg/d, 300 kg/yr and 1 kg/t of product, independent of the local situation). At existing sites, those measures are implemented when they can achieve an optimum performance, considering the ratio between environmental benefits and costs; for details see Section 3.1.5.2.3.

3.3.2.3.4.2 Chemical precipitation

Description
Precipitation is a chemical reaction to form particulates (i.e. solid precipitate) that can be separated from the water portion by an additional process, such as sedimentation (Section 3.3.2.3.3.4), air flotation (Section 3.3.2.3.3.5), filtration (Section 3.3.2.3.3.6) and, if necessary, followed by MF or UF (Section 3.3.2.3.3.7). 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).

In the case of heavy metals, precipitation is generally carried out as close as possible to the source in order to avoid dilution. In contrast, the precipitation of phosphorus is usually carried out during final treatment (see Section 3.3.2.3.5.7).

A precipitation facility usually consists of one or two stirred mixing tanks, where the agent causing precipitation (i.e. precipitation chemicals) and possibly other chemicals (e.g. flocculants) 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) to precipitate heavy metals;
- dolomite to precipitate heavy metals;
- sodium hydroxide to precipitate heavy metals;
- sodium carbonate to precipitate heavy metals;
- calcium salts (other than lime) to precipitate sulphate or fluoride;
- sodium sulphide to precipitate heavy metals, e.g. arsenic, mercury, chromium, cadmium, nickel;
- polyorganosulphides to precipitate mercury.

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

- ferrous and ferric salts;
- aluminium sulphate;
- polymers (cationic, anionic or non-ionic);
- polyorganosulphides.

Conventional hydroxide precipitation for removing heavy metals from waste water exhibit the drawbacks given below.

- Some metal hydroxides tend to redissolve upon increasing the pH value above a certain critical value. This is called 'amphoterism'. When the waste water contains a mixture of heavy metals, the pH ideally suited for efficient removal of one metal may be unfavourable for efficient removal of the others.
- Metal hydroxide precipitation is incomplete in the presence of chelating agents such as EDTA.

The precipitation of metals as hydroxides is most commonly used. Lower concentrations can be reached if metals are precipitated as sulphides [63, VITO 2010].

Achieved environmental benefits
Precipitation is used to remove metals and other inorganics (e.g. phosphorus or phosphate compounds), fats, oils, greases and some other organic compounds from waste waters [227, CWW TWG 2009] [234, US EPA 2000].

Achievable emission levels for heavy metals vary greatly, depending on the particular situation possible. Variables may include:

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

Chemical precipitation has a high yield and the achievable final concentration is determined by the compound's solubility product. It is difficult to determine the final concentration for a combination of pollutants due to the interaction of substances with each other. Achievable end concentrations for single metals with $Ca(OH)_2$ as the reagent are 1–10 mg/l and approximately 0.1–1 mg/l for copper, lead, silver and cadmium with S^{2-} [63, VITO 2010].

Some performance data can be found in the OFC BREF [105, COM 2006].

Cross-media effects
The precipitants usually have to be disposed of as sludge. Often this sludge is classified as chemical waste, at least if heavy metals are involved. This waste may contain carbonates,

fluorides, hydroxides (or oxides), phosphates, sulphates, and sulphides of heavy metals depending on the precipitating agent used.

Sources of noise are pumps and sludge removal facilities. Appropriate measures for noise control should be taken (e.g. equipment enclosure).

If the release of volatile and odorous substances can be expected (e.g. when precipitating metals as sulphides, H_2S can occur), precipitation should be operated in closed tanks or covered basins with ducts to gas abatement facilities (see Section 3.5.5.4).

Consumables are given in Table 3.35.

Table 3.35: Consumables associated with chemical precipitation

Consumable	Amount
Precipitation agent (e.g. lime, dolomite, ferrous and ferric salts, ferrous sulphate/sodium sulphide, aluminium sulphate, polymers, polyorganosulphides)	Dependent on contaminant load Theoretical consumption of some precipitation agents in kg to precipitate one kg of metal ions is: CaO: 0.88 for Cu, 0.96 for Ni, 1.62 for Cr, 0.86 for Zn $Ca(OH)_2$: 1.16 for Cu, 1.26 for Ni, 2.13 for Cr, 1.14 for Zn NaOH: 1.26 for Cu, 1.36 for Ni, 2.31 for Cr, 1.22 for Zn
Energy (kWh/m^3)	NI
NB: NI = no information provided. *Source:* [83, TI 2007]	

Operational data

<u>Monitoring</u>

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

A chemical precipitation facility in Germany receives wash water streams from two waste incineration plants (from the first off-gas washing step where only the highly concentrated waste water streams are pretreated; the less concentrated washing streams discharge to the central WWTP without any pretreatment) and a minor contribution of one point source from speciality inorganic production for the removal of heavy metals before discharging into a central WWTP. Pretreatment is only effective for highly concentrated waste water streams. The central WWTP located on the chemical site treats waste water streams originating from more than 250 production plants. As a result of chemical precipitation, 95 tonnes of sludge are produced per month, which is about 700 kg dry sludge per kg heavy metal removed (3 500 kg wet sludge per kg heavy metal removed). The sludge generated needs to be disposed of safely and this also requires the consumption of chemicals and energy. Sludge generation is an important cross-media effect and chemical precipitation is only effective for the treatment of highly concentrated waste water streams.

The operational data of another plant are given in Table 3.36 (raw data have been provided based on monthly loads from the year 2009, the average monthly waste water flow is reported to be 9 418.5 m^3).

Table 3.36: Operational data from a pretreatment facility for WWTP #06

Parameter	Concentration before treatment (µg/l)	Concentration after treatment (µg/l)	Abatement efficiency (%)
Mercury	680	< 5	99
Cadmium	36	< 15	58
Copper	6 160	< 50	99
Nickel	1 070	< 50	95
Lead	710	< 25	97
Chromium total	390	< 50	87
Zinc	5 600	< 50	99
Source: [227, CWW TWG 2009].			

Applicability

Precipitation can be applied at different stages of the waste water stream, for example:

- directly at the source to remove heavy metals most effectively to avoid dilution by unloaded streams;
- as the central treatment technique for the removal of phosphates, sulphate and fluoride, provided inadequate dilution is not expected;
- to remove phosphates 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 optimum conditions are usually determined on a case by case basis.

Application limits and restrictions are given in Table 3.37.

Table 3.37: Application limits and restrictions associated with chemical precipitation

Issue	Limits/restrictions
pH adjustment	Optimum pH range for heavy metals, phosphate, fluoride (generally pH 9–12) with lime. A broader pH range is available with sodium sulphide. 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 are given in Table 3.38.

Table 3.38: **Advantages and disadvantages associated with chemical precipitation**

Advantages	Disadvantages
General • Chemical precipitation is a well-established technique with ready availability of equipment and many chemicals • Some treatment chemicals, especially lime, are very inexpensive • Completely enclosed systems are often conveniently self-operating and low-maintenance, requiring only replenishment of the chemicals used	General • Competing reactions, varying levels of alkalinity and other factors typically make calculation of proper chemical dosages impossible. Therefore, frequent jar tests are necessary for confirmation of optimal treatment conditions. Overdosing can diminish the effectiveness of the treatment • Chemical precipitation may require working with corrosive chemicals, increasing operator safety concerns • The addition of treatment chemicals, especially lime, may increase the volume of waste sludge by up to 50 % • Large amounts of chemicals may need to be transported to the treatment location • Polymers can be expensive
With lime as an agent • Prevention of increased 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	With lime as an agent • Operating problems associated with the handling, storage and feeding of lime [1, Metcalf and Eddy 1991] • Increase of sludge amount due to an excess of calcium hydroxide • Maintenance problems [1, Metcalf and Eddy 1991]
For sodium sulphide • Precipitation occurs over a broad pH range • Decrease in amount of sludge (about 30 % in volume, compared to lime treatment) • Decrease in amount of chemicals used (about 40 %, compared to lime treatment) • Produces lower metal levels in treated effluent • No pretreatment or post-treatment needed • Highly efficient at removing suspended and dissolved metals from a waste water stream	For sodium sulphide • Generation of hydrogen sulphide when the batch becomes acidic by failure • Odour problems associated with sodium sulphide
Source: [1, Metcalf and Eddy 1991] [234, US EPA 2000].	

Economics

The costs are expected to be similar to those presented for the sedimentation process associated with flocculation (see Section 3.3.2.3.3.4) and are given in Table 3.39. The operating and maintenance costs will depend on the agents used in the precipitation process and on the required quantity with regard to the matrix composition.

Table 3.39: **Economics associated with chemical precipitation**

Type of costs	Costs
Investment costs	EUR < 0.03 per m^3 ([1])
Operating costs	NI
([1]) See Table 3.13.	
NB: NI = no information provided.	

Driving force for implementation
Driving forces for implementation include material recovery as well as reduction of pollutants discharged to the receiving water.

Example plants
Chemical precipitation is a technique used in many industrial installations for treating waste waters.

Reference literature
[1, Metcalf and Eddy 1991] [63, VITO 2010] [83, TI 2007] [105, COM 2006] [216, Viavattene et al. 2010] [222, CWW TWG 2013] [227, CWW TWG 2009] [234, US EPA 2000]

3.3.2.3.4.3   Crystallisation

Description
Crystallisation is closely related to precipitation. In contrast to precipitation, the precipitate is not formed by a 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 3.26.

Source: [37, Giesen and van der Molen 1996]
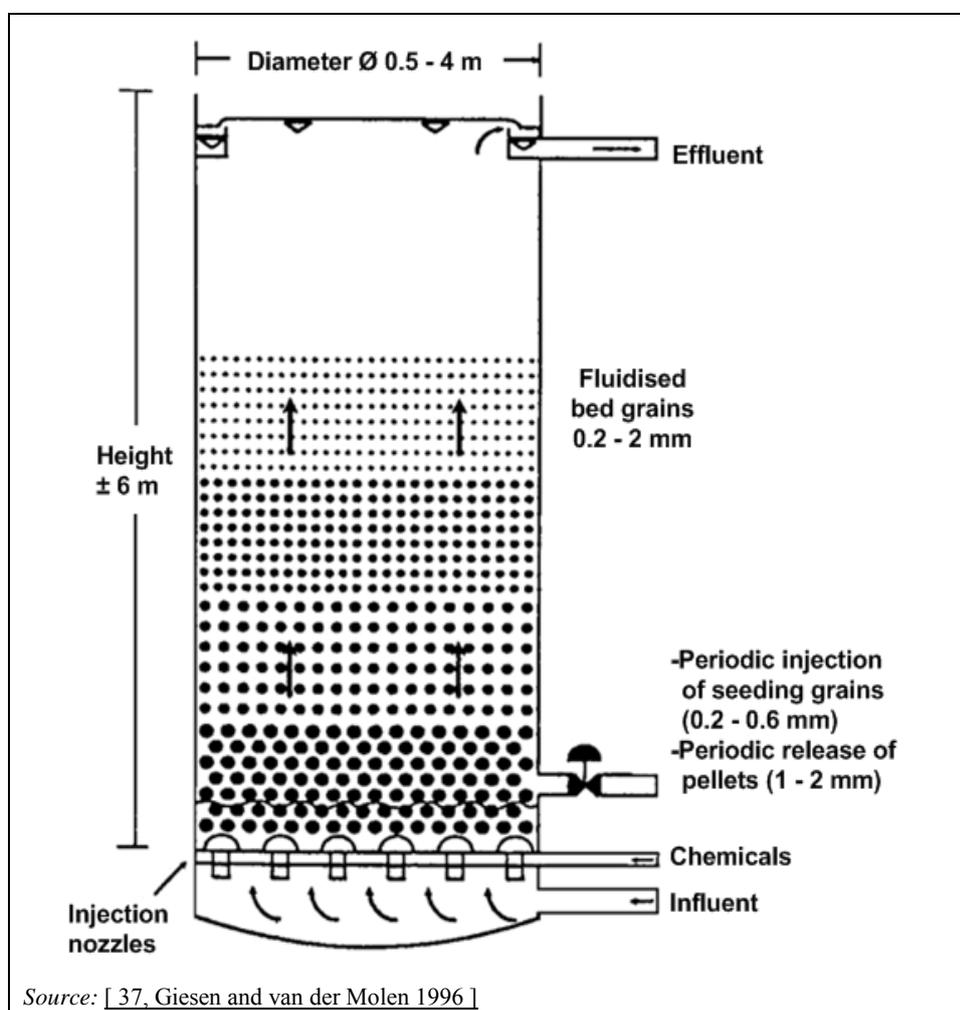
Figure 3.26: Principle of crystallisation process

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 a recirculation pump.

The velocity of the influent waste water (40–120 m/h) keeps the pellets in a fluidised state [37, Giesen and van der Molen 1996]. 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 (5 000–10 000 m^2/m^3) so that, in a fast and controlled reaction, almost all the anion or metal content crystallises on the pellets. Periodically, some of the pellets are 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, because:

- fluctuations in the influent flow and composition are easily eliminated;
- all kinds of waste water with concentrations in the range of 10–100 000 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 backwashing of conventional sand filters. The carry-over removed by the filter is redissolved 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 3.27.

Source: [37, Giesen and van der Molen 1996]
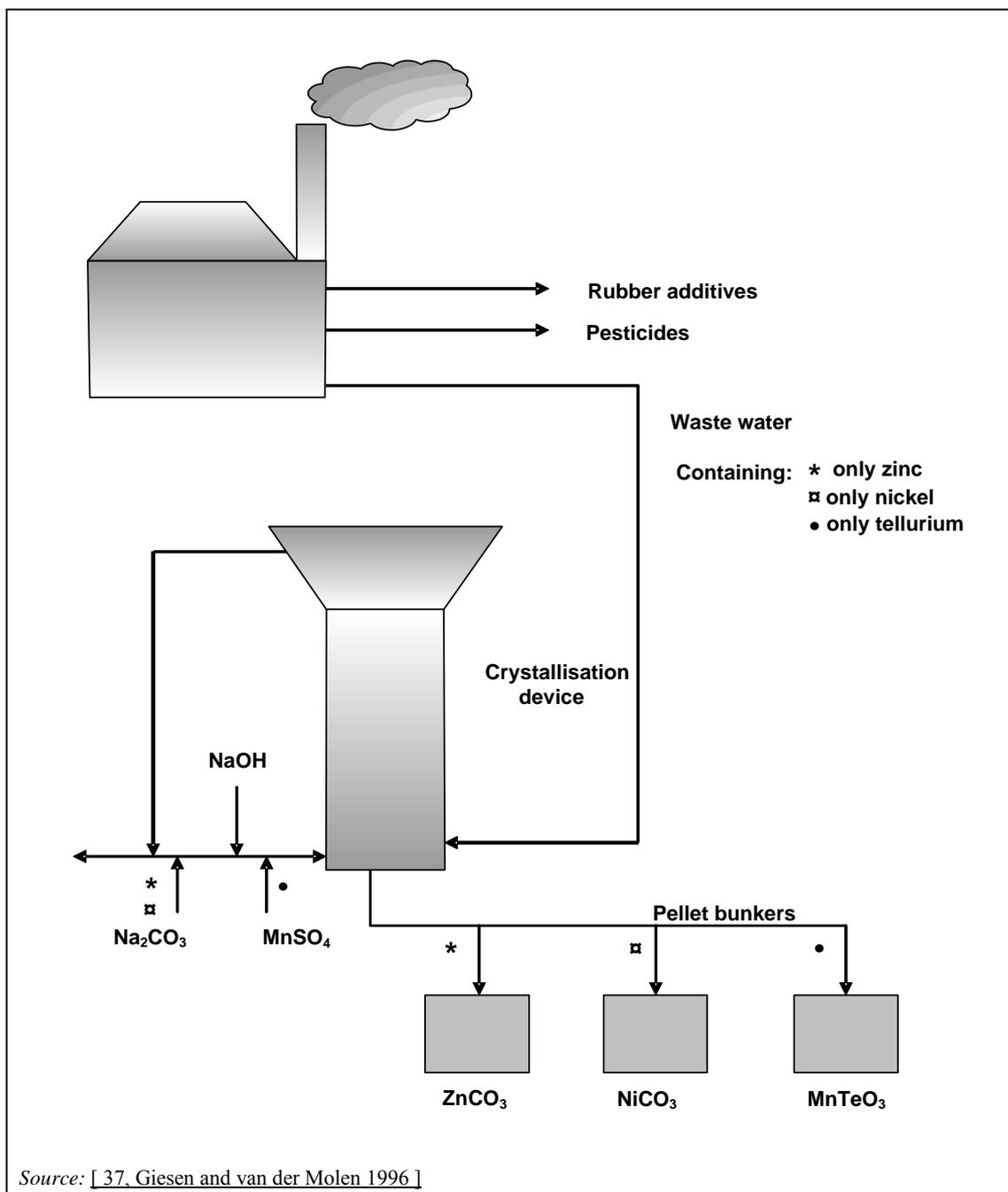
Figure 3.27: Multi-purpose application of crystallisation in a chemical production

Achieved environmental benefits
The main purpose of crystallisation is the abatement or recovery of heavy metals. Emission levels associated with crystallisation are given in Table 3.40.

Table 3.40:   Emission levels associated with crystallisation

Parameter	Emission level (mg/l)	Agent	Comments
Zinc	1	Soda, caustic soda	Feed 50–250 mg/l, pH 10
Nickel	1	Soda, caustic soda	Feed 50–250 mg/l or 1 000 mg/l, pH 10
Tellurium	1	Manganese sulphate, caustic soda	pH 9, after filtration
Aluminium	20	Sulphate, caustic soda	Feed 50–400 mg/l
Source: [37, Giesen and van der Molen 1996].			

Cross-media effects

To achieve good removal results, the reagents necessary to form the precipitates are normally added in an overdosage. 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 [37, Giesen and van der Molen 1996]. 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 given in Table 3.41.

Table 3.41:   Consumables associated with crystallisation

Consumable	Amount
Crystallisation chemicals	NI
Energy (kWh/m^3)	220 kWh (case study for the implementation of a grain reactor for fluoride removal from a flow with a volume of approximately 10 m^3/h) [63, VITO 2010]
NB: NI = no information provided.	

Operational data

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.

Applicability

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 [37, Giesen and van der Molen 1996]:

- recovery of zinc, nickel and/or tellurium in the production of rubber additives, with feed concentrations between 50 ppm 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 ppm 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. Meanwhile, metals normally abstracted as carbonates, hydroxy carbonates, hydroxides, sulphides, phosphates, sulphates, fluorides, etc. are generally removed as calcium salts [37, Giesen and van der Molen 1996].

Application limits and restrictions are given in Table 3.42.

Table 3.42: **Application limits and restrictions associated with crystallisation**

Issue	Limits/restrictions
Flow rate	0.1–10 000 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 are given in Table 3.43.

Table 3.43: **Advantages and disadvantages associated with crystallisation**

Advantages	Disadvantages
- Compact and flexible units, thus enabling modular set-up and tailor-made material 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 almost insoluble salts - Reagents restricted to non-hazardous substances - Total salt content of waste water is not decreased

Economics

The economic situation is presented in Table 3.44.

Table 3.44:   Economics associated with crystallisation

Type of costs	Costs/kg ([1])	Comments
Costs:		
Investment costs	NI	—
Operating costs	NI	—
Depreciation	USD 3–25 (EUR 2.4–20)	Depending on capacity
Chemicals	USD 0.5–2.5 (EUR 0.4–2.0)	Depending on concentration
Energy	USD 0.25 (EUR 0.20)	—
Staff	NI	1 hour per day
Maintenance	NI	3–5 % of investment
Benefits:		
Reuse	USD 0–14.5 (EUR 0–11.4)	Depending on anion or metal
Reduction of chemical waste	USD 2–8 (EUR 1.6–6.3)	Depending on concentration in sludge
Reduction of operating costs for precipitation	USD 0.5–3 (EUR 0.4–2.4)	In the case of pretreatment
Saving on investment for precipitation plant	USD 3–12 (EUR 2.4–9.4)	In the case of final treatment
Reduction of discharge fee	USD 30–40 (EUR 24–31)	In the case of final treatment
([1]) Costs per kg recovered anion or metal. Average currency conversion rate for 1996: EUR/USD = 1.275. NB: NI = no information provided. *Source:* [37, Giesen and van der Molen 1996].		

A case study for the implementation of a grain reactor for fluoride removal from a flow with a volume of approximately 10 m^3/h indicates investment costs of EUR 500 000 [63, VITO 2010]).

Driving force for implementation
The driving force for implementation is the recovery and/or reduction of heavy metals from waste water streams.

Example plants
Sectors where crystallisation is used include the chemical industry, the ore processing industry (metals), and the food industry (phosphate from potato processing) [63, VITO 2010]. Examples in the chemical industry include:

- recovery of zinc, nickel and/or tellurium in the production of rubber additives [37, Giesen and van der Molen 1996];
- recovery of nickel and aluminium in the production of elastomers [37, Giesen and van der Molen 1996];
- recovery of sodium sulphate in the production of chlor-alkali [110, COM 2014];
- recovery of sodium nitrate in the production of metal catalysts (WWTP #05) [137, LAWA 2008].

Reference literature
[37, Giesen and van der Molen 1996] [63, VITO 2010] [110, COM 2014] [137, LAWA 2008]

3.3.2.3.4.4   Chemical oxidation

3.3.2.3.4.4.1   General

Description
Chemical oxidation is the conversion of pollutants by chemical-oxidising agents other than oxygen/air or bacteria into similar but less harmful or hazardous compounds and/or to short-chained and more easily degradable or biodegradable organic compounds. Chemical oxidation is also used to degrade organic compounds causing odour, taste, colour [159, Baig 2006] and for disinfection purposes [227, CWW TWG 2009]. A side effect of some chemical oxidation processes is to precipitate reduced compounds (e.g. iron, manganese, sulphides).

Chemical-oxidising agents include:

- chlorine;
- sodium or calcium hypochlorite;
- chlorine dioxide;
- permanganate [159, Baig 2006];
- ozone (with or without UV light);
- hydrogen peroxide;
- hydroxyl radicals generated by hydrogen peroxide (known as Advanced Oxidation Process) in combination with:
  - ferrous salts (Fenton's agent [119, Pignatello et al. 2006]), see Section 3.3.2.3.4.4.2 for a detailed description of an oxidation technique involving hydrogen peroxide and a ferrous ion catalyst,
  - ozone,
  - UV light,
  - Pressure,
  - temperature.

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

- Oxidation processes are normally operated at pressures of up to 0.5 MPa [22, BMU/LAWA 2000]. 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 stored or transported and has to be generated on site. After treatment, surplus ozone has to be eliminated, e.g. using a catalyst system based on manganese oxide. Safety requirements to handle ozone are strict.
- With hydrogen peroxide as an oxidising agent, a GAC adsorber (see Section 3.3.2.3.4.10) may be 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, e.g. by sulphite.

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

Achieved environmental benefits
For hydrogen peroxide as an oxidising agent, the COD elimination of various organic substances as a function of hydrogen peroxide utilisation is illustrated in Table 3.45.

Table 3.45: COD elimination of various substances as a function of H$_2$O$_2$ utilisation

Substance	Dosage H$_2$O$_2$/COD (%) (^{1})	COD elimination (%) (^{2})	H$_2$O$_2$ utilisation (%)
Morpholine	100	20	20
2-Aminoethanol	100	37	37
Diethylene glycol	100	45	45
Polyethylene glycol	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

(^{1}) Percentage of stoichiometric amount.
(^{2}) Percentage of initial value.
Source: [251, Ullmann's 2000].

Abatement efficiencies for chlorine/hypochlorite-based techniques are given in Table 3.46.

Table 3.46: Abatement efficiencies of chemical oxidation using chlorine/hypochlorite-based techniques

Pollutant	Abatement efficiency (%)	Oxidising agent	Comments
TOC	> 90 (^{1})	Chlorine/hypochlorite	Feed about 1 g/l TOC
AOX	80 (^{1})	Chlorine/hypochlorite	Feed about 40 mg/l AOX
Oil	75–90 (^{2})	Hypochlorite	Feed 10–20 mg/l oil
Phenols	45–70 (^{2})	Hypochlorite	Feed 150–200 mg/l phenols
PAHs	30–55 (^{2})	Hypochlorite	Feed 1–2 mg/l PAHs
Cyanide	NI	NI	—
Sulphide	NI	NI	—
Sulphite	NI	NI	—

(^{1}) [22, BMU/LAWA 2000].
(^{2}) Risk of chlorinated side product formation [227, CWW TWG 2009].
NB: NI = no information provided.

When waste water with refractory organic compounds is treated, the main task is to break these compounds into more easily biodegradable/less harmful compounds (i.e. predigestion). Bearing that in mind, the most practical source of performance feedback 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 (e.g. biological treatment).

Cross-media effects
While oxidation with ozone and/or hydrogen peroxide does not normally create a transfer problem 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 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 given in Table 3.47.

Table 3.47:   Consumables associated with chemical oxidation

Consumable	Amount
Oxidising agent	2.8 mg O_3/g of cyanide 40–400 mg O_3/l to remove phenols 500 mg – some g per litre of waste water treated to remove odour, colour, and COD in chemical effluents
Agent to destroy surplus oxidant	Manganese oxide (MnO_2)
Energy (kWh/m^3)	NI
Energy for ozone production (kWh/kg O_3)	7–13 from oxygen [159, Baig 2006] 13–20 from dry air [159, Baig 2006]
NB: NI = no information provided.	

An example of consumables can be found in the OFC BREF [105, COM 2006].

Operational data
Monitoring
During the oxidation process, a thorough monitoring of operation parameters is crucial, for example:

- pH;
- reduction potential;
- ozone concentration (ozone concentrations of 15–20 % in the air are very unstable and tend to decompose [3, Environment Agency (England and Wales) 1997]);
- oxygen content in the gas phase (for safety reasons);
- content of surplus oxidant in the effluent;
- AOX content in the effluent, if chlorine-based agents are used.

Applicability
Chemical oxidation is normally applied when the waste water contains contaminants that are not readily biodegradable, or not biodegradable at all (e.g. inorganic compounds), might disturb or overload 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 (e.g. ethyl *tert*-butyl ether, methyl *tert*-butyl ether);
- phenols, chlorophenols;
- monocyclic aromatic hydrocarbons (BTEX);
- polycyclic aromatic hydrocarbons (PAHs);
- halogenated organic compounds (e.g. chlorinated solvents);
- dyes (with Fenton's agent);
- pesticides;
- cyanides;
- sulphides;
- sulphites;
- heavy metal complexes.

Some of these contaminants are biodegradable to a greater or lesser extent depending upon the optimisation of the biological process in a downstream WWTP and can alternatively be treated with specially adapted microorganisms. 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, or close to, 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 to remove refractory COD, odorous compounds or colour pigments, or for disinfection purposes.

Oxidation with chlorine or sodium chlorite can be used under special conditions to remove organic contaminants, even halogenated organic compounds. 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 halogenated organic compounds from the organic content in the waste water stream.

Application limits and restrictions are given in Table 3.48.

Table 3.48: Application limits and restrictions associated with chemical oxidation

Issue	Limits/restrictions
UV irradiation	• High turbidity results in poor transmission of UV • Ammonia content needs to be low, competes with the organics-consuming radicals [3, Environment Agency (England and Wales) 1997] • Substances that tend to foul will decrease the efficiency • Incomplete oxidation or formation of intermediate contaminants can hamper the effectiveness of the process

Advantages and disadvantages are given in Table 3.49.

Table 3.49: Advantages and disadvantages associated with chemical oxidation

Advantages	Disadvantages
• Inorganic substances can be treated • Waste water with refractory COD concentrations over a range of some g/l down to less than 1 μg/l can be treated [17, US Navy 1998] • 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 [251, Ullmann's 2000]) • 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 halogenated organic compounds possible, when halogen compounds are used as an oxidising agent • High cost per unit removal [227, CWW TWG 2009] • Formation of chloramines when hypochlorite is reacted with waste streams containing NH_3 [227, CWW TWG 2009]

Economics

The different chemical oxidation processes can be cost-effective in a given operating range (flow, initial contaminant concentration). For example, a chemical oxidation based on UV light 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, and UV/hydrogen peroxide/ozone, entail relatively high investment and operating costs and require more extensive waste water pretreatment than irradiation-free processes.

The overall costs for chemical oxidation are expected to be high. Operating costs are highly variable because of the chemicals required and these costs are the preponderant costs for the chemical oxidation treatment, which makes it difficult to predict the cost implication of this

treatment. Investment costs are also very variable depending on the technique used. This will also affect the type of chemical used and the final operating costs [216, Viavattene et al. 2010].

Driving force for implementation
Driving forces for implementation include relieving the subsequent biological treatment of COD/AOX loads that could have a disturbing, inhibiting or toxic effect.

Example plants
Chemical oxidation is used at various OFC plants [105, COM 2006].

Reference literature
[3, Environment Agency (England and Wales) 1997] [17, US Navy 1998] [22, BMU/LAWA 2000] [105, COM 2006] [119, Pignatello et al. 2006] [159, Baig 2006] [216, Viavattene et al. 2010] [227, CWW TWG 2009] [251, Ullmann's 2000]

3.3.2.3.4.4.2   Wet oxidation with hydrogen peroxide

Description
Wet oxidation with hydrogen peroxide is a technique used to treat waste waters contaminated with organic compounds in order to achieve COD (TOC) reduction, or to increase the biodegradability of the contaminants contained in the waste waters.

The technique is based on the Fenton reaction. It consists of the oxidation of the organic matter contained in the waste waters by hydroxyl radicals. These radicals are formed from the reaction of hydrogen peroxide with a ferrous ion (i.e. Fe^{2+}) catalyst. The reaction is carried out in the acidic medium and with mild conditions of temperature (100–150 °C) and pressure (2–4 bar) using catalyst and hydrogen peroxide formulations as an oxidant.

The use of a strong oxidant (radical) at higher temperatures and pressures than in the conventional Fenton reaction significantly improves the grade of mineralisation of most organic compounds with short residence times and more efficient usage of hydrogen peroxide.

The future of the technique though is to be based on its use as a pretreatment followed by a biological treatment.

The reaction products depend on the waste water content and include:

- carbon dioxide from organic content;
- water from organic content;
- nitrate from nitrite and organics which contain nitrogen;
- ammonium form amino-compounds;
- chloride from chlorinated organic compounds;
- sulphate from sulphides, sulphites and sulphonates;
- phosphate from compounds which contain phosphorus.

The typical wet oxidation with hydrogen peroxide plant consists of the following subsystems.

- The acidification tank.
- Heat exchangers (in order to optimise the heat of reaction; the fresh effluent is partially heated by the treated water).
- Continuous stirred tank reactor (or reactors to reach the necessary residence time).
- Post-treatment system. The pH of the treated effluent is adjusted to slightly basic which allows for catalyst precipitation.
- Decanter, where the flocculation agent is added to achieve the catalyst and solids separation by flocculation and decantation from the treated water.
- Centrifuge or filter press (where the inert waste sludge is finally dehydrated).

A schematic of the wet oxidation with hydrogen peroxide technique is shown in Figure 3.28.

Source: [147, FMC 2008]
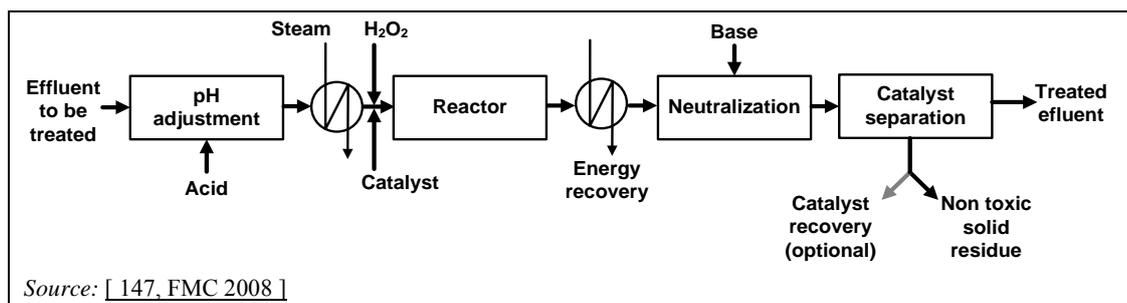
Figure 3.28: The wet oxidation with hydrogen peroxide technique

Wet oxidation with hydrogen peroxide can be used to treat various kinds of organic waste water (in particular refractory compounds), e.g. halogenated organics, chloramines, AOX, fats and greases, phenols, monocyclic and polycyclic aromatics, naphthalene, polychlorinated biphenyls, dyes, pesticides and herbicides.

The wet oxidation with hydrogen peroxide technique is used in fine/speciality and large volume chemical production plants, petrochemical plants, the production of dyes, plastics and rubbers, as well as installations generating poorly biodegradable waste waters, like landfill leaching and waste waters from waste processing plants.

Achieved environmental benefits
Achieved environmental benefits include:

- COD (TOC) reduction;
- increase in the biodegradability of the contaminants contained in the waste waters;
- reduction of the amount of specific compounds in the treated water, e.g.:
  ◦ chlorinated aromatics,
  ◦ phenol and naphthene derivatives,
  ◦ organic N compounds (nitro and amino),
  ◦ organic S compounds,
  ◦ organic P compounds,
  ◦ organic Cl compounds,
  ◦ inorganic compounds such as nitrite and sulphite are oxidised to nitrate and sulphate.

The environmental performance of the technique is not only measured by the TOC, COD or specific compound reduction, but also taking into account biodegradability improvement for further biological treatment. Moreover, additional reduction could be achieved at the cost of excessive consumption. Compromise must be attained in order to optimise costs. An example of the efficiency of the wet oxidation with the hydrogen peroxide technique achieved at one plant is given in Table 3.50.

Table 3.50: **Example of the efficiency of the wet oxidation with hydrogen peroxide technique achieved at one plant**

Pollutant	Abatement efficiency (%)	Comments
COD	70–99	—
TOC	70–99	—
Black colour	100	—
Phenol	99.8	Inlet 900 mg/l
Acetone	99.9	Inlet 100 mg/l
Toxicity	99.5	Inlet 1 200 Equitox
Pesticides	> 99	Inlet 2 400 ppm
Toluene	98.5	Inlet 13 ppm
Aniline	95	Inlet 2 ppm
Benzothiazole	> 99	Inlet 120–200 ppm
MBT	> 99	Inlet 12–30 ppm
Ethanol	> 99	Inlet 1 000 ppm
Source: [147, FMC 2008].		

The removal of specific organic compounds using the wet oxidation with hydrogen peroxide technique is indicated in Table 3.51.

Table 3.51: **Abatement efficiencies associated with wet oxidation with hydrogen peroxide**

Industry	Major organic species	Controlled pollutant	Initial concentration (mg/l)	Abatement efficiency (%)
Dietary fibre	Pyrazole, pyridine, indole, quenoline, trizone	TOC	7 800	98
Polyurethane	Anilines, nitrobenzenes, nitrophenols, phenols	TOC	10 000	98
Chemicals	Alcohols, organic acids	TOC	67 000	99
Polymers	Organic and inorganic sulphides	Sulphides	9 900	100
Waste water treatment	Phenols, chlorophenols	Phenol	15 282	100
Chemicals	Alcohols, organic acids	TOC	27 030	91
Adhesive	Toluene	TOC	2 272	95
Plastics	Methyl isobutyl ketone	TOC	11 000	99
Chemicals	Phenols	TOC	40 300	97
Groundwater	MTBE	MTBE	166	100
Pharmaceutical	HEPES	TOC	5 530	97
Source: [147, FMC 2008].				

Cross-media effects
The main cross-media effects of the wet oxidation with hydrogen peroxide technique relate to the need for pH control and to the generation of sludge.

Depending on the intensity of the oxidation treatment, the water effluent may need downstream treatment (e.g. biological). Depending on the waste water influent, the gaseous effluent may contain traces of acetic acid and acetone generated by the process, which need to be treated in downstream waste gas facilities. Inorganic solids formed after the filtration step (approximately 1 kg/m^3) is disposed of.

Consumables are given in Table 3.52.

Table 3.52:   Consumables associated with wet oxidation with hydrogen peroxide

Consumable	Amount
Hydrogen peroxide	2.2 ppm per ppm of influent COD
Energy (kWh/m^3)	NI
NB: NI = no information provided.	

The energy consumption is variable and depends on the amount of TOC to be removed and on the amount of hydrogen peroxide used. For H_2O_2 addition higher than 2 % or TOC removed higher than 3 000 mg/l, the process surpasses the autothermal area. Excess heat of the reaction can be used if recovery heat exchangers are installed.

Operational data
Typical reaction parameters are given in Table 3.53.

Table 3.53:   Typical reaction parameters for the wet oxidation with hydrogen peroxide technique

Parameter	Range	Comments
Temperature range	100–150 °C	—
Pressure range	2–5 bar	—
pH	1–5	Typically 2–4
H_2O_2 (%)	1–3 %	Max. 4 % per step in a multi-serial reactor
Residence time (in minutes)	30–60	NI
Catalyst (mg/l)	10–100	Fe; other possible catalysts are Cu and Mn

Monitoring
During the process, a thorough monitoring of operation parameters is crucial, including:

- influent pH;
- pH in the reactor;
- catalyst feeding;
- influent flow rate;
- reaction temperature and pressure (process and safety reasons);
- COD and peroxide concentration in the influent and in the effluent;
- oxygen content in the gas phase generated (for safety reasons).

Applicability
The wet oxidation with hydrogen peroxide technique is applicable to any chemical plant having to treat waste waters with organic loads.

The technique can be applied as a stand-alone treatment or combined with a more economical biological treatment, depending on the oxidant's dose.

Application limits and restrictions are given in Table 3.54.

Table 3.54: Application limits and restrictions associated with wet oxidation with hydrogen peroxide

Issue	Limits/restrictions
Contaminant concentration	• Recommendable for TOC ranges of 100–20 000 mg/l • Advantages not relating to economics for lower than 100 mg/l of TOC except for added-value recycling purposes • Quantities of TOC higher than 10 000 mg/l require a multi-reactor system or dilution • No more than 4 % H_2O_2 can be added per reactor vessel. Additions of H_2O_2 between 2 % and 4 % are thermally self-supported [227, CWW TWG 2009]. • If fluoride concentration is > 5 mg/l, special materials should be used
Insoluble complexes	Careful attention should be paid to insoluble complexes that can be formed between ferrous salt and organic compounds causing plugging in heat exchangers and efficiency losses
Unsuitable contaminants	The wet oxidation with hydrogen peroxide technique is susceptible to scavenging of hydroxyl radicals by non-target substances (e.g. natural organic matter, halides), and is unsuitable for certain compounds (such as perchlorinated compounds) that in principle resist attack by hydroxyl radicals [119, Pignatello et al. 2006]. For such compounds, specific laboratory oxidation suitability tests of should be carried out [227, CWW TWG 2009].

Advantages and disadvantages are given in Table 3.55.

Table 3.55: Advantages and disadvantages associated with wet oxidation with hydrogen peroxide

Advantages	Disadvantages
• Compared to other bulk oxidants, hydrogen peroxide is inexpensive, and easy to handle, and poses no lasting environmental threat since it readily decomposes to water and oxygen. Likewise, iron is comparatively inexpensive, safe, and does not pose a threat to the environment • Waste water with refractory TOC concentrations over a range of 20 g/l to less than 100 g/l can be treated • Organic contaminants can be removed or transformed to less hazardous compounds • Large flow rate fluctuations can be managed • Short residence time and therefore small vessel volume is required. Easy to integrate into existing treatment plants • Can be integrated with other treatments • Solid waste is made up of inert metal salts	• Limitations of wet oxidation with hydrogen peroxide for waste water treatment stem mainly from the need for pH control and sludge generation • Hydrogen peroxide requires an appropriate (well-defined by standards) storage and handling to avoid risk of explosive decomposition • Sludge formation

Economics

The approximate investment costs depending on the flows of waste water that need treatment are given in Table 3.56.

Table 3.56: **Economics associated with wet oxidation with hydrogen peroxide**

Type of costs	Costs	Comments
Investment costs	300 000	For 1 m^3/h of waste water
	350 000	For 2 m^3/h of waste water
	400 000	For 5 m^3/h of waste water
	700 000	For 10 m^3/h of waste water
	900 000	For 20 m^3/h of waste water
Operating costs	EUR 1–1.5/kg COD abated, or EUR 3–30/m^3	—
Source: [147, FMC 2008].		

Driving force for implementation
Driving forces for implementation include relieving the subsequent biological treatment of COD/AOX loads that could have a disturbing, inhibiting or toxic effect.

Example plants
Examples of production processes where wet oxidation with hydrogen peroxide is used include the production of pesticides, the pharmaceutical industry, the epichlorohydrin process, the petrochemical industry, the production of aromatic hydrocarbons, organic peroxide production, chemical dyes for the leather industry, the tanning industry, auxiliary products for the foundry industry, and waste management of third party industries.

An example of a chemical plant using the wet oxidation with hydrogen peroxide technique is Repsol Química in Tarragona, Spain.

Reference literature
[119, Pignatello et al. 2006] [147, FMC 2008] [227, CWW TWG 2009]

3.3.2.3.4.4.3   Wet air oxidation

Description
Wet air oxidation is the reaction of oxygen in the aqueous phase under high pressure and temperature, used to increase the solubility of oxygen in water [194, Martínez-Huitle and Ferro 2006]. The reaction often takes place in the presence of catalysts. Reaction products are dependent on the waste water content and include:

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

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

- low-pressure wet air oxidation;
- high-pressure wet air oxidation.

The corresponding distinctions in temperature and pressure are also associated with major differences in process engineering factors, material considerations and plant safety requirements [251, Ullmann's 2000].

Typical properties of the two variants are given in Table 3.57.

Table 3.57: Typical properties of two variants of wet air oxidation

Parameter	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 [7, Joziasse and Pols 1990]:

- the reactor vessel according to the applied pressure and temperature, including:
  - a well-mixed, vertical bubble column without mechanical mixing,
  - a horizontal reactor with agitated compartments in series,
  - a deep shaft reactor,
  - 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 preheating facilities for the waste water input.

The material requirement for the hot parts of the plant is very high. Suitable equipment for temperatures of < 160 °C needs to be enamelled or lined with PTFE, and metal parts to be operated at temperatures of 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 the cold parts [251, Ullmann's 2000].

An example of the low-pressure wet air oxidation process is shown in Figure 3.29.
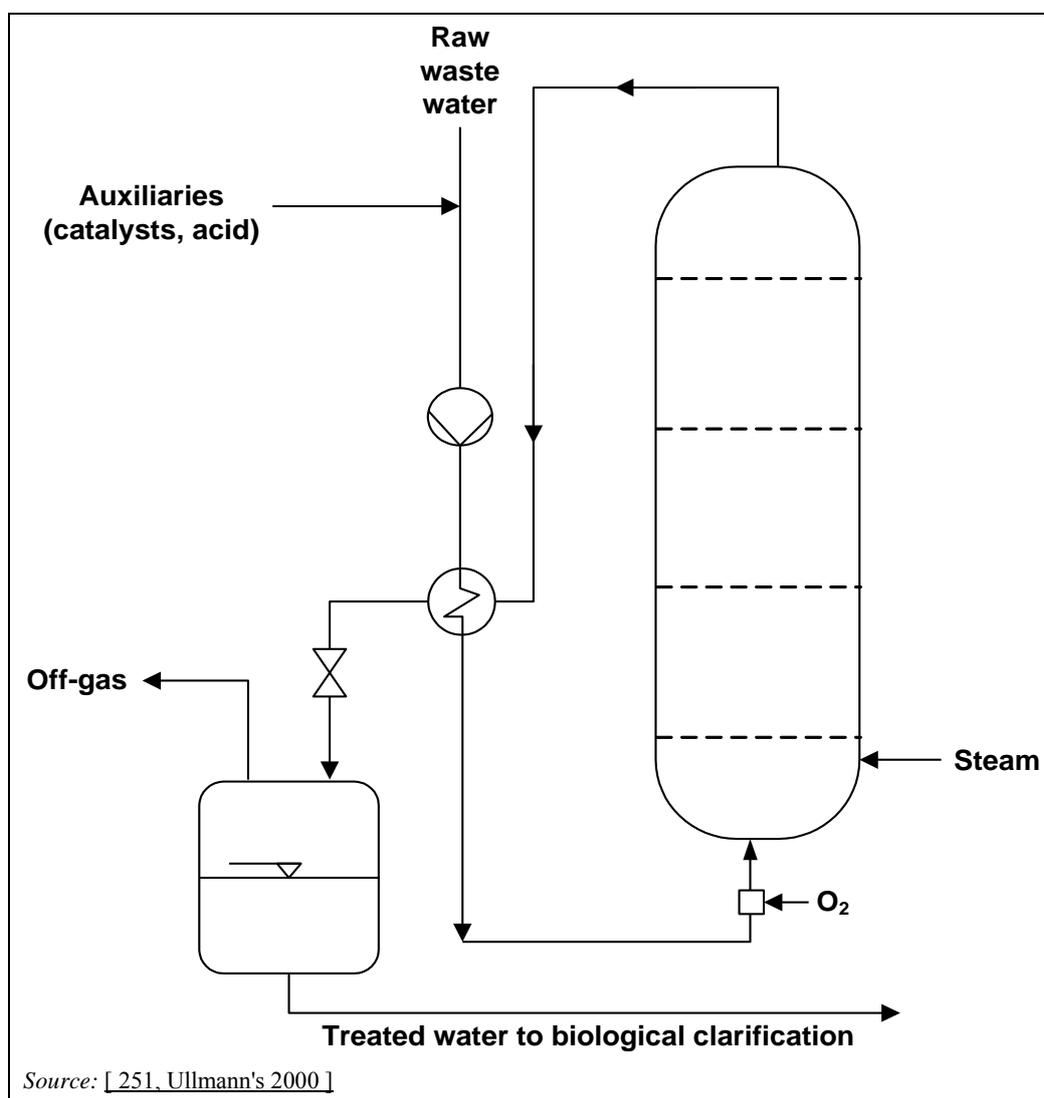
Figure 3.29: Flow diagram of a Loprox facility operated at 120–200 °C and 0.3–2.0 MPa with a retention time of < 3 h

Achieved environmental benefits
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 compounds into easily degradable compounds;
- send this waste water to a downstream (central) biological WWTP.

Thus performance 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 data given in Table 3.58 are reported.

Table 3.58: Abatement efficiencies associated with low-pressure wet air oxidation

Parameter	Performance	Comments
COD	60–90 % ([1])	Example: 85 % reduction by wet air oxidation (190 °C, 2 MPa), followed by 90 % reduction after the biological clarification step, in total 98 % COD reduction ([2])
	50 % ([3])	90 % after biological treatment
AOX	60–> 90 % ([1]) ([2])	Reaction temperature of 190 °C
BOD/COD	increase from 0.1 to 0.5 ([2])	Reaction temperature of 190 °C
Sodium sulphide	< 1 mg/l ([4])	Initial concentration 30 g/l, 160 °C, 0.9 MPa
([1]) [22, BMU/LAWA 2000]. ([2]) [251, Ullmann's 2000]. ([3]) [87, UBA DE 2000]. ([4]) [76, Ecker and Winter 2000].		

For the high-pressure variant, the data in Table 3.59 are reported.

Table 3.59: Abatement efficiencies associated with high-pressure wet air oxidation

Pollutant	Abatement efficiency (%)	Comments
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]) [76, Ecker and Winter 2000]. ([2]) [87, UBA DE 2000]. ([3]) [251, Ullmann's 2000].		

As an example of the application of high-pressure wet air oxidation to low TOC concentrations, the removal of pesticides is reported in Table 3.60.

Table 3.60:   Example of achieved emission levels of pesticides with high-pressure wet air oxidation

Contaminant	Influent concentration (µg/l)	Effluent concentration (µg/l)
Aldrin	500	< 50
DDT	21 000	< 300
Endosulfan	18 400	291
Endrin	3 600	< 100
2,4-Dichlorophenol	180	< 3.1
Source: [3, Environment Agency (England and Wales) 1997]		

Cross-media effects

Under adverse conditions, the 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 the stripping of waste water, and gas scrubbing, biofiltration or thermal/catalytic oxidation of waste gas.

Wet air oxidation implies the consumption of air or oxygen and energy. 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.

Operational data

Monitoring

During the whole process, a thorough monitoring of operation parameters such as pressure, temperature and oxygen content is vital to ensure faultless functioning.

Applicability

Wet air oxidation is applied to waste water which contains contaminants that are either not readily biodegradable or might disturb the biological process in a downstream biological WWTP, or which have properties which are too harmful to allow them to be released into an ordinary sewer system. It is also used for sludge treatment (see Section 3.4.2). The substances preferably considered for this technique using the low-pressure variant are:

- 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 [251, Ullmann's 2000];
- phenol and naphthene derivatives that are converted at 120–150 ºC;
- chlorinated aromatics that are converted in a catalysed process at 120–190 ºC.

The substances using the high-pressure variant are:

- organic nitro compounds that are converted to nitrogen;
- organic amino compounds or aromatics which contain nitrogen hetero atoms that are converted to ammonia;
- organic sulphur compounds that are converted to sulphate;
- organic phosphorus compounds that are converted to phosphate;
- chlorinated organic compounds that are converted to hydrochloric acid.

Examples of production processes where wet air oxidation is applied include [87, UBA DE 2000]:

- the production of dyes and intermediates;
- the oxidation of aromatic sulphonates;
- the production of derivatives of phenol or naphthol;
- the 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 are given in Table 3.61.

Table 3.61: Application limits and restrictions associated with wet air oxidation

Issue	Limits/restrictions
Contaminant concentration	• No advantage for low COD concentrations (oxidation rates of most organic constituents are too low to allow for an efficient application [194, Martínez-Huitle and Ferro 2006]); recommendable for COD concentrations of between 5 000 mg/l and 50 000 mg/l [87, UBA DE 2000], concentrations of between 6 000 mg/l and 8 000 mg/l being autothermal [251, Ullmann's 2000] • Concentrations of over 100 000 mg/l demanding dilution [3, Environment Agency (England and Wales) 1997] • With the high-pressure variant, COD concentrations of above 50 000 mg/l are required to equal the total energy demand of the process [251, Ullmann's 2000] • Fluoride concentrations: < 5 mg/l for high-pressure variant, < 10 mg/l for low-pressure variant; higher concentrations require pretreatment, e.g. by precipitation with calcium salt and subsequent filtration [87, UBA DE 2000] • Fluoride concentrations consistent with the solubility product of calcium fluoride are sufficient to initiate corrosion at pH < 5 (high-pressure variant) [251, Ullmann's 2000] • Salt loads have to be minimised as far as possible, at least with the high-pressure variant, because of corrosion [22, BMU/LAWA 2000], e.g. [87, UBA DE 2000]: - 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 (see Section 3.3.2.1) upstream of the oxidation facilities

Advantages and disadvantages are given in Table 3.62

Table 3.62: Advantages and disadvantages associated with wet air oxidation

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 [22, BMU/LAWA 2000]

Economics

Wet air oxidation treatments are usually compared with the incineration treatment both from a treatment and an economic point of view. The overall cost is expected to be extremely high for several industries. The main reason is the specific equipment required to treat at high pressure and temperature. Operating and maintenance costs are higher than the investment costs. The spectrum of the cost per m^3 depends on the COD to be treated. Economics for the wet air oxidation technique are given in Table 3.63 [216, Viavattene et al. 2010].

Table 3.63: Economics associated with wet air oxidation

Type of costs	Costs	Comments
Investment costs	EUR 2–12 million EUR 10–40 per m^3	For a treatment capacity of less than 200 m^3/d
Operating and maintenance costs	NI	At 100 °C
	NI	At 200 °C
	EUR 40–80 per m^3	Up to EUR 100 per m^3 if post-treatment of effluent is necessary
NB: NI = no information provided.		
Source: [216, Viavattene et al. 2010].		

Driving force for implementation
Driving forces for implementation include relieving the subsequent biological treatment of COD/AOX loads that could have a disturbing, inhibiting or toxic effect.

Example plants
Chemical oxidation is used at various OFC plants [105, COM 2006] and LVOC plants (e.g. Repsol Química, Tarragona, Spain).

Reference literature
[3, Environment Agency (England and Wales) 1997] [7, Joziasse and Pols 1990] [22, BMU/LAWA 2000] [76, Ecker and Winter 2000] [87, UBA DE 2000] [105, COM 2006] [194, Martínez-Huitle and Ferro 2006] [216, Viavattene et al. 2010] [251, Ullmann's 2000]

3.3.2.3.4.5 Chemical reduction

Description
Chemical reduction is the conversion of pollutants by chemical reducing agents into similar but less harmful or hazardous compounds. Common chemical reducing agents include:

- sulphur dioxide;
- sodium hydrogen sulphite/metabisulphite;
- ferrous sulphate;
- sodium sulphide and sodium hydrogen sulphide;
- urea or amidosulphonic acid (at low pH).

These chemicals 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 a chemical precipitation unit.

The design of the treatment reactor depends on its special purpose. The basic facility is a continuous stirred tank reactor, 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 reduction potential control, may alleviate this problem. Chemical reduction plants need not be especially sophisticated and costly. Where continuous/automatic processing is appropriate, investment costs might be higher, but are normally compensated for by lower operating costs. The process is performed in fully automatic units operated by monitoring a surrogate indicator parameter, typically the reduction potential.

Storage facilities need to be provided for the reducing agents, bearing in mind the potentially hazardous nature of these substances.

Achieved environmental benefits
No information provided.

Cross-media effects
No particular environmental problems are to be considered. The arising gases are captured and ducted to downstream waste gas treatment facilities.

Chemical reduction implies the consumption of a reducing agent, and in some cases also the consumption of energy and/or of another chemical agent to destroy the surplus reducing agent. The consumption of reducing agents depends on the contaminant load; the consumption of chemicals to destroy surplus reactants depends on the processing quality.

Operational data
Monitoring
The reaction is monitored and controlled by independent control loops and includes:

- caustic/acid addition by pH control;
- reducing agent addition by control of the reduction potential.

The effluent needs to be checked for surplus reducing agents.

Applicability
Chemical reduction is applied to waste water that contains contaminants that are not readily removable or have properties which are too harmful to allow them to be released into a common sewer system. The target contaminants are inorganic compounds: chemical reduction 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 a low pH.

The frequent downstream operation in connection with chemical reduction is chemical precipitation.

Application limits and restrictions are given in Table 3.64.

Table 3.64:   Application limits and restrictions associated with chemical reduction

Issue	Limits/restrictions
Substances	The number of affected inorganic substances is limited
pH and reduction potential	Performance highly dependent on pH and reduction potential, thus strict control of these parameters is essential
Reaction conditions	Good stirring is required

Advantages and disadvantages are given in Table 3.65.

Table 3.65:   Advantages and disadvantages associated with chemical reduction

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

Economics
Combined with high contaminant concentrations and the large amount of reducing agent, there might be other treatment techniques that are more cost-effective.

Driving force for implementation
The driving force for implementation is to convert difficult to treat pollutants into readily removable ones for their downstream treatment and removal.

Example plants
No information provided.

Reference literature
No reference literature provided.

3.3.2.3.4.6   Chemical hydrolysis

Description
Basically, hydrolysis is a destructive technique. It is a chemical reaction in which organic and inorganic constituents react with water, breaking them 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.

Normally, hydrolysis processes are operated at ambient pressure and temperature. When a high temperature is required, the reactor has to be fitted with a heat exchanger system with preheating 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 acids or bases have 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.

Achieved environmental benefits
Abatement efficiencies are heavily dependent on the chemical structure of the compound, as well as on the pH and the temperature of the waste water. Quantitative degradation can be achieved, but pilot studies are required to obtain the individual treatment conditions.

Since the elimination of refractory organic contents and/or inhibitors of subsequent biological treatment is the main goal, the performance 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 (see Section 3.5.5.4).

Chemical hydrolysis implies the consumption of chemicals and energy.

Operational data
Monitoring
During the hydrolysis process, a thorough monitoring of operating parameters is crucial, such as:

- temperature;
- pH;
- pressure;
- residence time.

 The effluent should be checked for specific degraded compounds and surplus acid/base agents.

Applicability
Chemical hydrolysis is applied to waste water streams which contain contaminants that are not readily biodegradable, or that might disturb the biological process in a downstream biological WWTP or have properties which are too harmful to allow them to be released into a common sewer system. Examples of such contaminants are:

- halogenated organic compounds;
- pesticides;
- organic cyanides;
- organic sulphides;
- organophosphates;
- carbamates;
- esters;
- amides.

Frequent operations in connection with chemical hydrolysis include:

- chemical neutralisation;
- chemical oxidation;
- precipitation.

The reaction is highly dependent on the chemical structure of the chemical compounds, as well as on the pH and the temperature of the waste water, which may have the following effect:

- an increase in temperature entails an increase in the hydrolysis rate;
- a low or high pH can increase the reaction rate, depending on the reagent, e.g. phosphoric acid esters and chlorinated organic compounds are preferably hydrolysed under alkaline conditions;
- catalysts can increase the reaction rate.

Application limits and restrictions are given in Table 3.66.

Table 3.66: Application limits and restrictions associated with chemical hydrolysis

Issue	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	Not suitable for substances requiring extreme operating conditions
Water solubility	Low solubility in aqueous media can limit the applicability

Advantages and disadvantages are given in Table 3.67.

Table 3.67:   Advantages and disadvantages associated with chemical hydrolysis

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

Economics
No information provided.

Driving force for implementation
The driving force for implementation is to convert difficult to treat pollutants into readily removable ones for their downstream treatment and removal.

Example plants
No information provided.

Reference literature
[22, BMU/LAWA 2000]

3.3.2.3.4.7   Nanofiltration (NF) and reverse osmosis (RO)

Description
A membrane process is the permeation of a liquid through a membrane, to be segregated into permeate that passes through the membrane and concentrate that is retained. The driving force of this process is the pressure difference across the membrane.

Nanofiltration (NF) and reverse osmosis (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.

NF membranes allow water, single valence ions (e.g. fluorides, sodium and potassium chloride) and nitrates to pass through, while retaining multiple valence ions (e.g. sulphate and phosphates). The salts become concentrated and are discharged as a concentrated brine. RO membranes have the smallest pore size ($< 0.002\,\mu m$) used in liquid/liquid separation. They allow water to pass through and retain the solute (e.g. salts, metal ions and certain organics). The salts become concentrated and are discharged as a concentrated brine [161, WEF 2008].

The typical characteristics of NF and RO membranes are illustrated in Table 3.68.

Table 3.68:   Characteristics of NF and RO

Parameter	Technique	
	NF	**RO**
Pore size (μm) ([1])	0.001–0.01	< 0.002
Operating pressure (MPa)	0.5–3 ([2]) 0.5–1 ([3])	1–8 ([3])
Cut-off size (nm) ([2])	> 1 200–1 000 g/mol	< 1 000 g/mol
Minimum particle size removed ([3])	200–400 Daltons Multivalent ions	50–200 Daltons All ions
Permeate flow (l/(m^2×h))	< 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]) [161, WEF 2008]. ([2]) [254, Ullmann's 2009]. ([3]) [152, Schippers et al. 2004].		

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 include cellulose acetate and 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 flows across the membrane;
- the post-treatment section where the permeate is prepared for reuse or discharge, and the concentrated brine is collected for further work-up or disposal.

As an example, a typical RO arrangement is illustrated in Figure 3.30.

Membrane units are arranged as modules either in parallel (to provide the necessary hydraulic capacity) or in series (to increase the degree of efficiency).

Source: [1, Metcalf and Eddy 1991]
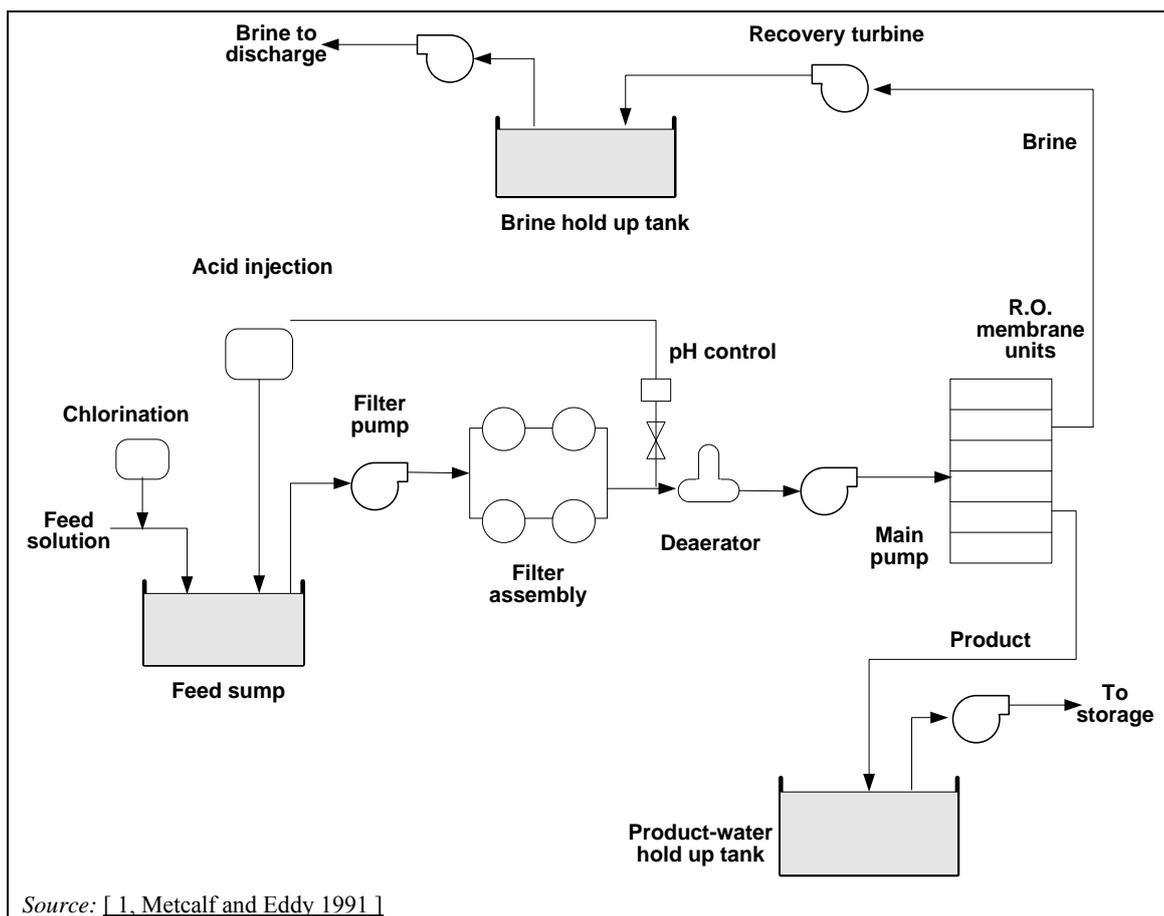
Figure 3.30: RO arrangement

Achieved environmental benefits
Achieved environmental benefits are given in Table 3.69.

Table 3.69: Abatement efficiencies associated with NF and RO

Pollutant	Abatement efficiency (%)	
	NF	RO
Inorganic mercury	> 90 ([1])	NI
Organic mercury	> 90 ([1])	NI
Cadmium compounds	> 90 ([1])	NI
Tetrachloromethane	96 ([1])	NI
Ethylene dichloride	71 ([1])	NI
Trichlorobenzene	96 ([1])	NI
Perchloroethene	90–92 ([1])	NI
Atrazine	> 70 ([1])	84–97 ([1])
γ-Hexachlorocyclohexane	NI	99 ([1])
DDT	NI	100 ([1])
Aldrin	NI	100 ([1])
Dieldrin	NI	100 ([1])
Dichlorvos	NI	98 ([1])
Simazine	NI	95 ([1])
Trifluralin	NI	99 ([1])
Fenitrothion	NI	99 ([1])
Azinphos-methyl	NI	98 ([1])
Malathion	NI	99 ([1])
TOC	80–90 ([2])	NI
([1]) [3, Environment Agency (England and Wales) 1997]. ([2]) [248, UBA DE 1999]. NB: NI = no information provided.		

The use of NF or RO may also reduce water usage if the permeate is recycled/reused. Moreover, raw material consumption may be reduced if the concentrate is recycled/reused [110, COM 2014] [216, Viavattene et al. 2010].

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 [251, Ullmann's 2000]).

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 reused or recycled in the industrial process, thus reducing water input and discharge.

Consumables are given in Table 3.70.

Table 3.70: Consumables associated with NF and RO

Consumable	Amount	
	NF	RO
Membrane material	NI	NI
Chemicals for cleaning	NI	NI
Energy (kWh/m^3)	1–3 ([1])	1–3 ([1])
([1]) Low-pressure application, < 2.5 MPa [88, Mulder 1994]. NB: NI = no information provided.		

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.

Operational data

Monitoring

To ensure reliable operation, the pressure difference and flow across the membrane should be monitored continuously.

Applicability

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 reuse 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 reused. Examples are:

- desalination;
- final removal of, for example:
  - degradable compounds if biological treatment is not available,
  - heavy metals,
  - toxic compounds;
- 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 (see Section 3.3.2.3.4.11) or GAC adsorption (see Section 3.3.2.3.4.10).

Application limits and restrictions are given in Table 3.71.

Table 3.71:   Application limits and restrictions associated with NF and RO

Technique	Issue	Limits/restrictions
NF	Particle size	Restricted capacity to retain suspended particles with molecular weight < 200 Daltons (< 0.001 µm)
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 that tend to polymerise cause fouling
Both	Membrane material	Low thermal and chemical resistance limits their application to a restricted pH and temperature range (18–30 °C)

The specifications of the feed water are stricter in the case of RO than NF [63, VITO 2010].

Advantages and disadvantages are given in Table 3.72.

Table 3.72:   Advantages and disadvantages associated with NF and RO

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

Economics

The relevant investment costs are for the membranes and the pumping systems. These costs vary according to the pressure, the flow and the surface required [216, Viavattene et al. 2010].

Because of the RO membrane's fine pores, high operating pressures (690 kPa to 2 410 kPa) are required to separate metal ions from water, making electricity a major operating cost factor. The higher the salt concentration to be removed, the higher the operating costs will be. Another costly component of the RO process is membrane replacement. Even with anti-fouling measures, the membranes must be replaced approximately every five years throughout the life of the asset. The NF membranes operate at lower pressures than RO, resulting in lower operating costs. The operating pressures are about one-third to one-half of those required for RO. NF membranes must be replaced approximately every five years [161, WEF 2008]. There is no evidence of economy of scale for larger units. The operating and maintenance costs are higher than the investment costs and can be roughly equally divided between the energy for the pumping system, the membrane replacement and the membrane cleaning. Water and material savings are possible with this technique [216, Viavattene et al. 2010]. The costs of the technique are given in Table 3.73.

Table 3.73:   Economics associated with NF and RO

Technique	Investment costs	Operating and maintenance costs
NF	EUR 100 000 (^{1})–10 000 000 (^{2}) EUR < 0.1 per m^3	EUR < 0.4 per m^3 (^{3})
RO		

(^{1}) For treating less than 100 m^3/d of waste water (indicative).
(^{2}) For treating less than 10 000 m^3/d of waste water (indicative).
(^{3}) The operating and maintenance costs include the energy for the pumping system, the membrane replacement, and the membrane cleaning.
Source: [216, Viavattene et al. 2010].

The investment costs, including automated cleaning facilities, can be broken down approximately as follows [33, ETBPP 1997]:

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

The operating costs [33, ETBPP 1997] are 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 requirements.

They can be broken down approximately as follows [33, ETBPP 1997]:

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

Potential economic benefits may result from reduced water consumption and/or the recovery of raw materials [110, COM 2014] [216, Viavattene et al. 2010].

Driving force for implementation
The driving force for using NF and RO is the removal of toxic or inhibitory substances from waste waters.

Example plants
Sectors where NF is used include the removal of pesticides in groundwater and the softening of water.

The use of NF was reported for some WWTPs of the survey [222, CWW TWG 2013]:

- WWTP #06: NF as a central treatment to concentrate waste water streams from the production of dyes and intermediates originating from an OFC site. The permeate from the NF process is discharged to the WWTP whilst the concentrate is sent to a sludge incineration plant.
- WWTP #11: NF for the pretreatment of waste water from the production of alkanesulphonate.

Sectors where RO is used include the desalting of seawater and manure processing.

For WWTP #68, the use of RO as a pretreatment was reported [222, CWW TWG 2013].

Reference literature
[1, Metcalf and Eddy 1991] [3, Environment Agency (England and Wales) 1997] [33, ETBPP 1997] [63, VITO 2010] [87, UBA DE 2000] [88, Mulder 1994] [110, COM 2014] [152, Schippers et al. 2004] [161, WEF 2008] [216, Viavattene et al. 2010] [222, CWW TWG 2013] [251, Ullmann's 2000] [254, Ullmann's 2009]

3.3.2.3.4.8   Electrodialysis

Description
Electrodialysis is an electromembrane process in which ions are transported through ion-permeable membranes from one solution to another solution under the influence of a potential gradient. The electrical charges on the ions allow them to be driven through the membranes fabricated from ion exchange polymers. Applying a voltage between two end electrodes generates the potential field required for this. Since the membranes used in electrodialysis have the ability to selectively transport ions with positive or negative charges and reject ions of the opposite charge, useful concentration, removal, or separation of electrolytes can be achieved by electrodialysis.

A schematic of the technique is shown in Figure 3.31.
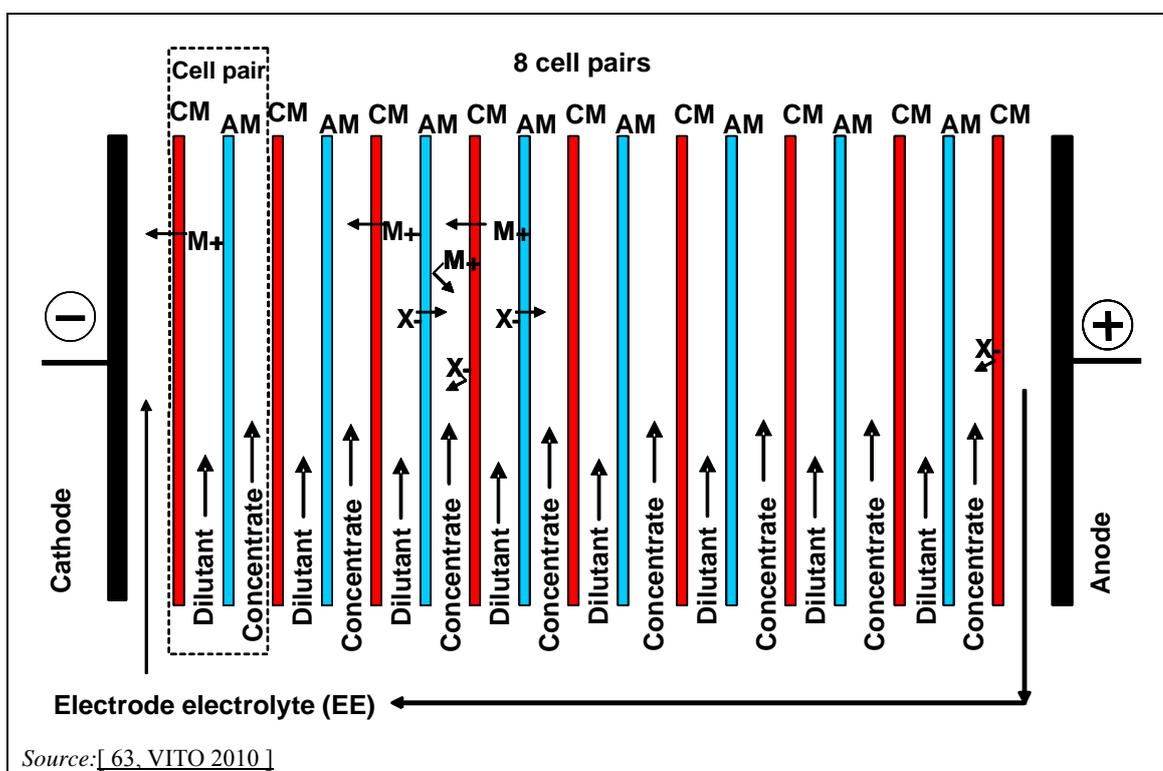
Figure 3.31: Electrodialysis

Anion-selective membranes (AM) and cation-selective membranes (CM) are placed between the anode (positive electrode) and the cathode (negative electrode). Under the influence of an electric field, anions will migrate in the direction of the anode and cations will migrate in the direction of the cathode. Anions are stopped by the CM and the cations by the AM, which creates a process flow that continues to reduce in ions (the dilutant) and a process that continues to increase in ions (the concentrate).

A combination consisting of a CM, an AM and both areas between these membranes is referred to as a cell pair (see area indicated by the dotted line in Figure 3.31). A cell pair is the basic unit of a stack, and is repeated *n* times (in the figure, *n*=8). In practice, a stack can contain hundreds of cell pairs.

Achieved environmental benefits
Electrodialysis allows for the removal of ions from process or waste waters and for their concentration so that they can be recycled/reused.

Cross-media effects
Electrodialysis requires the use of energy as well as support substances for pretreatments (e.g. flocculants, coagulants) as well as for membrane cleaning. Regular membrane cleaning with specific cleaning products (acids, bases, etc.) may be necessary in a number of cases. The average lifespan of electrodialysis membranes is between five and seven years.

Operational data
Monitoring
For parameter optimisation, a pilot electrodialysis process can be set up and equipped with specific instrumentation. Such instruments should measure pressure, volume, temperature, pH and conductivity. Once conditions have been optimised for a particular application, an industrial installation can, in principle, operate independently without extensive instrumentation, once the optimised parameters have been set to within the process limits. In this regard, an electrodialysis installation offers a fairly high operational certainty provided (incidental) membrane pollution is prevented.

Applicability
Advantages and disadvantages are given in Table 3.74.

Table 3.74:   Advantages and disadvantages associated with electrodialysis

Advantages	Disadvantages
• Relatively simple to operate and maintain	• Electrodialysis needs to be operated below the current density limit to be energy efficient

Economics
The major costs associated with electrodialysis are membrane and electricity costs. The current density limit is a limiting factor, because this limit being reached is linked to the splitting of water, and thus results in energy loss. As a general rule of thumb, in practice, a limit of 3 000 ppm of dissolved substances is regarded as the limit between cost-effective treatment via reverse osmosis (see Section 3.3.2.3.4.7) and electrodialysis. Thus, electrodialysis is cost-effective for dissolved substances of < 3 000 ppm and reverse osmosis is cost-effective for dissolved substances of > 3 000 ppm. Another argument in favour of electrodialysis could be the need for high feed recovery.

For an electrodialysis installation which treats 10 m^3 of waste water per day, originating from surface treatments in the metal industry, an investment of EUR 200 000 and operating costs of EUR 50 000 per year can be expected. Costs may vary greatly depending on the type of waste water to be treated.

Driving force for implementation
The driving force for using electrodialysis is the removal of toxic or inhibitory substances from waste waters.

Example plants
Electrodialysis is used in the food industry to demineralise milk products or sugar-related solutions. The amount of acid in fruit juice can also be reduced. In Japan, electrodialysis (combined with vaporisation) is used to prepare cooking salt from seawater.

Reference literature
[63, VITO 2010]

3.3.2.3.4.9   Electrolysis

Description
Electrolysis is a process in which an electrical current is applied to a liquid using inert electrodes and an electrical source, resulting in an effective electron transfer in the electrolyte, yielding chemical changes in the composition of the waste water. When the waste water is subjected to a current, the electrons are exchanged between the electrodes and the liquid. As a result, metal ions present in the waste water deposit on the cathode. The purified waste water then leaves the electrolysis cell and in many cases is reused. The efficiency of the technique can be improved by separating the cathode and the anode sections by the use of a membrane composed of a high charge density polymer. Therefore, the anion or the cation can be made selective by altering the charge of the membrane. As a result, this separation allows the conditions surrounding the electrodes to be individually optimised (e.g. pH correction), thus avoiding after-effects and increasing yields.

Achieved environmental benefits
Electrolysis allows for the removal of metal ions from process waters and/or waste waters and allows for the concentration of these metals so that they can be recycled/reused.

Cross-media effects
High consumption of energy when low final concentrations are required. Hydrogen gas and chlorine gas may form on the electrodes in the presence of (hydrochloric) acid. Side reactions such as the formation of gases and formation of HCN in cyanide must be prevented by pH correction.

Operational data
The ideal pH is determined by each application. Acids can be used to modify the pH in order to avoid the formation of metal hydroxides before metals deposit on the electrodes. Leach solution is used to prevent formation of hydrogen gas from hydrogen ions The retention period in the electrolysis cell is between five and thirty minutes.

The purification yield is very high and final metal ion concentrations of less than 0.1 mg/l are achievable. However, in order to achieve these levels, reactors with improved mass transfer and/or with high specific surface area should be used. When recuperating Pd and Ni from Pd-Ni alloy baths, the concentration of both metals is reduced to 20 mg/l. The remaining part can be recuperated using other techniques, such as ion exchange.

During the disintoxication of cyanides from galvanic baths, residual CN concentrations of less than 1 mg/l can be achieved with initial CN concentrations of 5 g/l. The remaining concentration can be further reduced using ion exchange.

Electrolysis is also used for the reduction of Cr(VI) to Cr(III) yielding residual Cr(VI) concentrations of less than 0.1 mg/l. In order to achieve high efficiencies (80 % to 90 %), the pH value must be kept less than 3 or 4.

Applicability
This method is most appropriate when a single metal pollutant is present in high concentrations in the waste water. The technique is also used for chemical oxidation/reduction and precipitation applications. For each target metal or organic compound that will be recuperated, attention should be given to the possible oxidation/reduction reactions. The type of electrode used is also important.

The advantage of this technique is that purified water as well as the metals deposited on the electrodes can be reused. In addition to metal removal, organic compounds in the waste water can also be degraded by oxidation and reduction with the exchange of electrons. For metal reuse, only one metal pollutant must be present in the waste water in a sufficiently high concentration as the recuperation of metal and water is difficult in complex mixtures. Also, the quality of the recuperated metal is affected by the inert anodes used as they partially dissolve. To avoid this, graphite anodes are used.

Electrolysis is mainly applied in the metal industry for the purification of rinse waters from pickling tanks or galvanic baths. The applications include recuperation of metals and used electrolytes, disintoxication of nitrite and Cr(VI) and silver recuperation from fixing baths in the graphics sector. This technique is also applicable for the treatment of leachate waters containing heavy metals.

Economics
The cost of an electrolysis installation is to a great extent determined by the type of electrodes that are used. A specific case has been provided to demonstrate this.

In a small plant for the recuperation of palladium from drag-out rinse tanks, 26 g/h Pd is recuperated. The cost of electricity amounts to EUR 0.75 per kg Pd. Investment costs amount to

EUR 93 per anode and EUR 13 per cathode, and eight anodes and seven cathodes are needed for each electrolysis cell. The anode is a Ti/RuO_2 electrode and the cathode is a three-dimensional electrode. The investment costs for the cell with electrodes are EUR 3 000 and a rectifier for the voltage amounts to approximately EUR 1 000.

Driving force for implementation
The driving force for implementation is the removal of metals from process waters and/or waste waters.

Example plants
No information provided.

Reference literature
[63, VITO 2010]

3.3.2.3.4.10   Adsorption

Description
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 given in Table 3.75 [251, Ullmann's 2000].

Table 3.75: **Commonly used adsorbents and their properties**

Adsorbent	Form	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Bulk density (g/l)
Activated carbon	Granular	500–1 000	0.3–0.8	300–550
	Powder	600–1 500	0.3–1.0	
Lignite coke	Granular, powder	200–250	< 0.1	Approximately 500
γ-Aluminium oxide	Granular, powder	300–350	0.4–0.5	700–800
Adsorber resins	Granules	400–1 500	Porosity 35–65 vol-%	650–700

Adsorption processes are divided into [251, Ullmann's 2000]:

*   mixing, usually used for batch-wise treatment;
*   percolation, applicable to continuous treatment, normally with a fixed-bed adsorber packed in two columns that are alternately on duty and undergoing backwashing;
*   pulse-bed or moving-bed process, as continuous percolation with waste water and adsorbent led countercurrent through the column.

Since the adsorbent-active surface is often liable to clogging and blockage, the waste water needs to be as free of solid content 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 3.32.

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.

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
Source: [251, Ullmann's 2000]
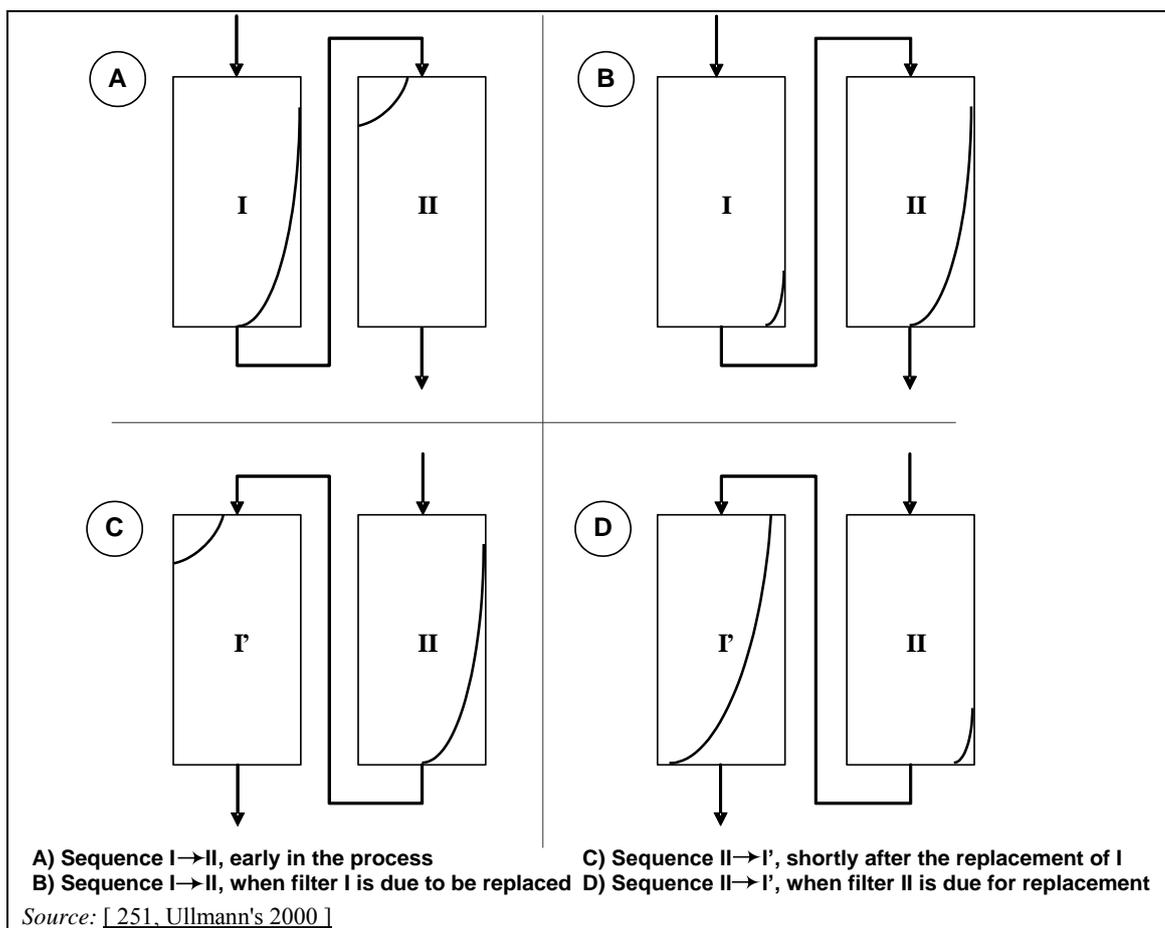
Figure 3.32: Operation of two adsorption columns connected in series

Achieved environmental benefits
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. Data collected during the development of the United States Effluent Limit Guidelines show that carbon can be extremely effective when used on individual waste water streams. However, the data showed the breakthrough of certain pollutants even with careful monitoring. In particular, in all cases, the concentrations of many heavy metals increased across the carbon units.

Abatement efficiencies associated with adsorption are given in Table 3.76.

Table 3.76: Abatement efficiencies associated with adsorption

Parameter	Abatement efficiency (%)			Comments
	GAC	PAC	Zeolite	
Inorganic Hg	80 ([1, 2])	NI	NI	Feed 29 µg/l
Organic Hg	80 ([1])	NI	NI	Low feed
γ-Hexachloro-cyclohexane	93 ([1])	NI	NI	Feed 7.7 µg/l
	NI	99 ([1])	NI	Feed 10 µg/l, PAC 85 mg/l
DDT	97 ([1])–99.9	NI	NI	—
Aldrin	88–93 ([1])	NI	NI	—
	NI	90–99 ([1])	NI	PAC 5–20 mg/l
Dieldrin	86–98 ([1])	NI	NI	—
	NI	99 ([1]) (0.1 µg/l)	NI	Feed 10 µg/l, PAC 126 mg/l
Atrazin	84 ([1])	NI	NI	Feed 0.61 µg/l
Endrin	NI	(< 0.1 µg/l) ([1])	NI	Feed 10 µg/l, PAC 70 mg/l
Dichlorvos	NI	99 ([1])	NI	—
Trichlorobenzene	NI	70–93 ([1])	NI	Feed 200 µg/l, PAC 20 mg/l
Fenitrothion	NI	99 ([1])	NI	—
Azinphos-methyl	NI	99 ([1])	NI	—
Ammonia	NI	NI	98 ([1]) (0.5 mg/l)	Feed 25 mg/l
COD	50 ([3, 4])	NI	NI	Moving-bed, feed 5 g/l
	67–75 ([4, 5]) (< 100 mg/l)	NI	NI	Feed concentration 300–400 mg/l
Phenols	75 ([3])	NI	NI	Moving-bed, feed 70 mg/l
	60–80 ([5]) (1–2 mg/l)	NI	NI	Feed concentration 5 mg/l
AOX	> 90 ([3])	NI	NI	Moving-bed, feed 60 mg/l

([1]) [3, Environment Agency (England and Wales) 1997].
([2]) 80 % removal not achievable for ionic, elemental form, but can be achievable for the inorganic particulate form [227, CWW TWG 2009].
([3]) [22, BMU/LAWA 2000].
([4]) COD removal is very dependent on the type of substance being removed [227, CWW TWG 2009].
([5]) [36, NOREC 2000].
NB: GAC = granular activated carbon; NI = no information provided; PAC = powdered activated carbon.

Powdered activated carbon (PAC) treatment systems are reported [17, US Navy 1998] to treat waste water with a COD higher than 60 000 mg/l, including toxic volatile organic compounds higher than 1 000 mg/l with a reduction of specific toxic organic chemicals to below the limit of detection, 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.

Granular activated carbon (GAC), lignite and activated aluminium oxide (when carrying an organic load) are thermally regenerated at temperatures up to 750–1 000 °C. Resins, zeolites and

activated aluminium oxide carrying inorganic loads 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 [3, Environment Agency (England and Wales) 1997] 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 have a period of at least six months between regeneration cycles.

The generation of off-gases with regeneration requires 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, PCDDs/PCDFs, heavy metals or dichlorobromopropane [17, US Navy 1998]

The regeneration of the zeolite adsorbent generates a concentrated stream of ammonia, which is sent to a conventional waste water treatment plant for biological treatment or, alternatively, which 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 given in Table 3.77.

Table 3.77: Consumables associated with adsorption

Consumable	GAC	PAC	Zeolite
Adsorbent	About 10 % loss per regeneration	0.1–1 g PAC/l of effluent or 10 g PAC/kg of suspended solids	NI
Chemicals for regeneration	NI	NI	NaCl/NaOH or lime 10–30 bed volumes ([1])
Energy (kWh/m^3)	NI	NI	NI
([1]) [3, Environment Agency (England and Wales) 1997]. NB: NI = no information provided.			

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.

Operational data
Monitoring
The input and output of the adsorber device have 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.

Applicability

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 [32, ETBPP (UK) 1996]:

- textiles and dyestuffs: removal of TOC, colour, dyes;
- petrochemical industry: 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 900–1 000 °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 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 are given in Table 3.78.

Table 3.78: Application limits and restrictions associated with adsorption

Issue	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	Increased efficiency with increasing carbon chain (free oil does not adsorb)
Branching of carbon chain	Decreased efficiency with increasing branching
Polarity	Decreased efficiency with high polarity
Solubility in water	Increased efficiency with high solubility (free oil does not adsorb)
Degree of dissociation	Decreased efficiency with increasing dissociation
Macromolecules	Decreased efficiency with macromolecular structure
([1]) [1, Metcalf and Eddy 1991]. ([2]) [7, Joziasse and Pols 1990]. *Source:* [227, CWW TWG 2009].	

The influence of polarity is demonstrated in Table 3.79.

Table 3.79: Typical performance characteristics of GAC adsorption with feed concentrations of about 1 000 mg/l

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	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
Source: [31, Kemmer 1988].		

Advantages and disadvantages are given in Table 3.80.

Table 3.80: Advantages and disadvantages associated with adsorption

Advantages	Disadvantages
• High removal efficiency (not lignite coke) • Enables the removal of refractory and/or toxic organic compounds (GAC, PAC, lignite coke, resins) • Usually low extra space requirements • 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 a major erosion problem (PAC) • Spent adsorbent has to be regenerated (high energy consumption) or disposed of (causing waste to be incinerated)

Economics

Economics associated with adsorption are given in Table 3.81.

Table 3.81: Economics associated with adsorption

	Investment costs	Operating and maintenance costs
GAC	EUR 50 000–1 000 000 ([1]) EUR 0.3–0.5 per m^3 (for up to 1 000 m^3/d) ([1])	EUR < 0.5 (for > 1 000 m^3/d and without taking into account the regeneration of adsorbent) ([1])
Active coal	EUR 1.28–2.06/kg ([2])	EUR 0.1/kg (removal cost for landfilling) ([2]) EUR 0.5/kg (removal cost as chemical waste ([2])
PAC	EUR 150 000 ([3])	NI
([1]) [216, Viavattene et al. 2010]. ([2]) Average total cost is EUR 0.05–4 per m^3 of water [63, VITO 2010]. ([3]) Investment costs of automatic dose installation [63, VITO 2010]. NB: NI = no information provided.		

Investment costs are relatively high for small units treating less than 100 m^3 per day. However, economy of scale is possible for larger units. Economy of scale is also observed for the operating and maintenance costs. Operating and maintenance costs are related to the replacement of the adsorbent bed. The regeneration or the destruction of the adsorbent are more expensive than the treatment itself [216, Viavattene et al. 2010]. As regeneration is relatively expensive, the technique is generally unattractive for highly contaminated streams that consume large amounts of carbon.

Driving force for implementation

The driving force for implementation is to meet the legal discharge requirements by removing organic contaminants (mainly those with refractory, toxic, coloured and/or odorous characteristics) and residual amounts of inorganic contaminants (e.g. nitrogen compounds, sulphides and heavy metals) from waste water streams.

Example plants

Sectors where adsorption is used include the textile industry, dry cleaning, the chemical industry, soil remediation, and the pharmaceutical industry.

The use of adsorption was reported for some WWTPs of the survey [222, CWW TWG 2013]:

• WWTP #06: pretreatment of waste water originating from an OFC site;
• WWTP #13: central activated carbon adsorption facility as a pretreatment (with on-site thermic regeneration) for waste water originating from the production of chlorinated nitroaromates containing high AOX concentrations;
• WWTP #15: central activated carbon adsorption facility for the treatment of mother liquors with high concentrations of (recalcitrant) TOC and AOX.

Reference literature

[1, Metcalf and Eddy 1991] [3, Environment Agency (England and Wales) 1997] [7, Joziasse and Pols 1990] [17, US Navy 1998] [22, BMU/LAWA 2000] [31, Kemmer 1988] [32, ETBPP 1996] [36, NOREC 2000] [63, VITO 2010] [216, Viavattene et al. 2010] [222, CWW TWG 2013] [227, CWW TWG 2009] [251, Ullmann's 2000]

3.3.2.3.4.11   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 a corrosion-resistant lining that contains the resin, usually as a packed column with several possible configurations;
- 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 the hollowing out of flow channels in the resin bed. It also acts as a 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, neutralising strong bases and converting neutral salts into their corresponding acids;
- weak acid cation exchangers, able to neutralise strong bases and used for dealkalisation;
- strong base anion exchangers, neutralising strong acids and converting neutral salts into their corresponding bases;
- weak base anion exchangers, neutralising strong acids and used for partial demineralisation.

The ion exchange operation cycle is comprised of:

- 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 rinse with a slow water flow, of 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.

Achieved environmental benefits
Typical effluent ion concentrations that can be achieved are in the range of 0.1–10 mg/l with influent concentrations of 10–1 000 mg/l.

Achieved environmental benefits associated with ion exchange are given in Table 3.82.

Table 3.82: Abatement efficiencies and emission levels associated with ion exchange

Parameter	Emission level (mg/l)	Abatement efficiency (%)	Comments
Effluent ion	0.1–10	80–99 ([1])	Influent concentrations of 10–1 000 mg/l
([1]) [63, VITO 2010].			

Cross-media effects

The regeneration of ion exchange resins results in a small volume of concentrated acid or salt solution, which contains 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. At a plant in Germany, the rinsing water from regeneration is reused in waste gas scrubbers.

Ion exchange implies the consumption of ion exchange resins, regeneration liquids, water for backwashing and rinsing, and energy for the pumps. The addition of other chemicals, e.g. to suppress microbiological fouling, may be necessary.

Sources of noise are the pumps, which can be enclosed.

Operational data

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 relevant ion(s).

Applicability

Ion exchange is applied to remove unwanted ionic and ionisable species from waste water, such as:

- 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, alkyl sulphates, 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 mg/l and 1 000 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 are given in Table 3.83.

Table 3.83:   Application limits and restrictions associated with ion exchange

Issue	Limits/restrictions
Ion concentration	High ionic strength can cause swelling of resin particles
Temperature	Thermal limits of anion resins are generally in the vicinity of 60 °C
Corrosive agents	Nitric acid, chromic acid, hydrogen peroxide, iron, manganese, and 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 are given in Table 3.84.

Table 3.84:   Advantages and disadvantages associated with ion exchange

Advantages	Disadvantages
• In principle all ions and ionisable species can be removed from aqueous liquids • It operates on demand, and is relatively insensitive to flow variations • High efficiency possible • Recovery of valuable species possible • Water recovery possible • A large variety of specific resins are available	• Prefiltration 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

Economics
Investment and operating costs depend on the nature of the feed stream. Economics associated with ion exchange are given in Table 3.85.

Table 3.85:   Economics associated with ion exchange

Type of costs	Costs	Comments
Investment costs	GBP 60 000 (EUR 73 000) ([1])	Packed height of 1 m and diameter of 1 m; vessel, valves and resin included
	+ GBP 20 000 (EUR 24 000) ([1])	For additional 0.5 m of diameter
Operating costs	NI	—
([1]) Average currency conversion rate for 1996: EUR/GBP = 0.8188. NB: NI = no information provided. *Source:* [32, ETBPP (UK) 1996].		

Driving force for implementation
The driving force for implementation is to remove undesired or hazardous ionic constituents from waste water streams.

Example plants
Sectors where ion exchange is used include surface treatment of metals, the printing industry, and the production of process water.

For WWTP #12, the use of chemical precipitation and ion exchange was reported for the removal of Hg from waste waters from the production of mercury salts (batteries) [222, CWW TWG 2013].

Reference literature
[22, BMU/LAWA 2000] [32, ETBPP 1996] [63, VITO 2010] [222, CWW TWG 2013]

3.3.2.3.4.12   Extraction

Description
Extraction means transferring soluble contaminants from the waste water phase into a solvent. Desirable properties for suitable solvents are:

- low solubility and low 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 (see Section 3.3.2.3.4.14);
- low toxicity;
- thermal stability.

Extraction is operated in columns where the waste water is brought into contact with the organic solvent in different ways, such as:

- countercurrent 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 (see Section 3.3.2.3.4.14). 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 and equipped with the necessary safety items to prevent emissions to air and soil.

Achieved environmental benefits
Achieved environmental benefits associated with extraction are given in Table 3.86.

Table 3.86:   Abatement efficiencies and emission levels associated with extraction

Parameter	Abatement efficiency (%)	Emission level (mg/l)	Comments
Phenols	99 ([1])	< 1	Feed 10 g/l
([1]) [22, BMU/LAWA 2000].			

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, and the former a ducted removal, e.g. to thermal/catalytic oxidation or adsorption.

After solvent recovery (distillation or rectification, see Section 3.3.2.3.4.14) the bottom residue that contains the extracted contaminants has to be disposed of as chemical waste, normally by incineration.

Extraction implies the consumption of solvents and energy.

Operational data
Monitoring
The input to the extraction unit has to be checked to prevent unwanted solids from entering, which might cause disturbances to the process or damages to the plant. Regular maintenance is necessary in order to prevent or detect solvent losses to the environment.

Applicability
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, adsorption or biological treatment are preferable. Extraction is often used as a pretreatment to adsorption and/or biological treatment units.

Examples of application of the technique are [22, BMU/LAWA 2000]:

- removal of phenol (phenosolvan process);
- recycling of metals, such as zinc;
- recycling of substances from mother liquors;
- removal of phosphoric acid esters;
- removal of chloroaromatics;
- pretreatment concentration of aromatic sulphonic acids.

Application limits and restrictions are given in Table 3.87.

Table 3.87: Application limits and restrictions associated with extraction

Issue	Limits/restrictions
Suspended solids	Waste water should be almost free of suspended solids and/or emulsions
Solvent	• Suitability of the solvent (see above) • Solvent loss entails costs and environmental impacts • Solvent regeneration can be very complicated and cost-intensive

Advantages and disadvantages are given in Table 3.88.

Table 3.88: Advantages and disadvantages associated with extraction

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

Economics
No information provided.

Driving force for implementation
The driving force for implementation is to remove and/or recover organic contaminants and metals from waste water streams.

Example plants
Extraction is a technique frequently used in the chemical industry, especially in the LVOC [104, COM 2003] and OFC sectors [105, COM 2006].

For WWTP #06, the use of extraction was reported as a central pretreatment for the concentration of waste water streams containing aromatic sulphonates originating from an OFC site (the raffinate is sent to a WWTP whilst the extract is sent to a sludge incineration plant) [222, CWW TWG 2013].

Reference literature
[22, BMU/LAWA 2000] [104, COM 2003] [105, COM 2006] [222, CWW TWG 2013]

3.3.2.3.4.13   Pertraction

Description
Process or waste water flows contaminated by organic substances such as aromatics or chlorinated hydrocarbons can be cleaned by pertraction. The pollutants are removed from the waste water by absorption into an organic extraction agent or extractant. Membranes form the interface between the waste water and the extractant. A schematic of the technique is presented in Figure 3.33.

In the pertraction process, therefore, the extractant is not added directly to the waste water, as in a conventional extraction process (see Section 3.3.2.3.4.12) and this offers important advantages over conventional extraction. It means that the often difficult and time-consuming separation between the water phase and the extractant phase is not necessary. The flows of waste water and extractant are flexible, and can be adjusted independently of one another, making process optimisation simpler and allowing a highly efficient contact between a large volume of (waste) water and a very small quantity of extractant. The pertraction installation can be of very compact construction, thanks to the high specific surface area and good mass transfer of the pertraction membrane modules.
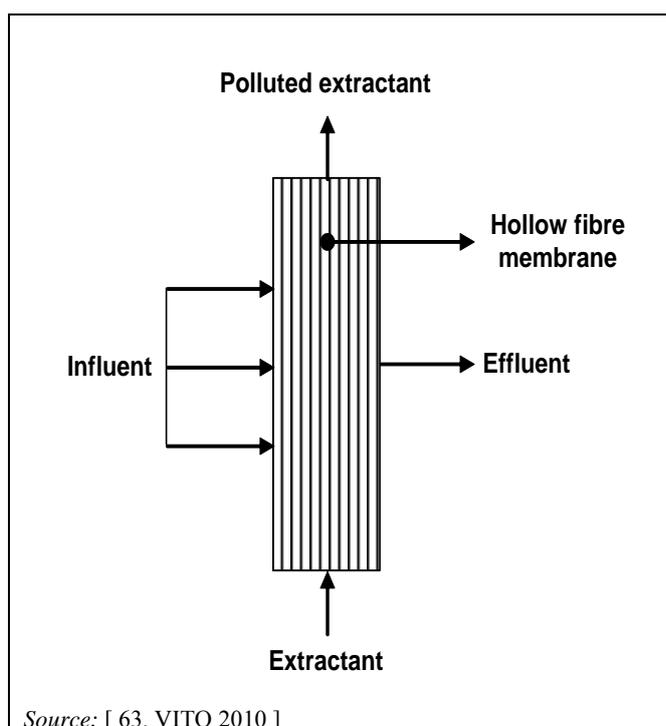
Figure 3.33: Pertraction

Achieved environmental benefits
The reduction of the emission of organic substances such as aromatics or chlorinated hydrocarbons to receiving waters is the achieved environmental benefit of this technique.

Pertraction can be used to remove a broad spectrum of organic compounds (e.g. pesticides, monocyclic aromatic compounds, PAHs).
The yield for removing hydrocarbons is generally high, also at low concentrations (ppb level). Values of more than 99.5 % can be achieved.

This process is particularly efficient for low pollution concentrations.

Cross-media effects
Spent extractant needs to be regenerated.

Operational data
A pertraction system consists of one or multiple membrane modules (membranes are normally in a hollow fibre configuration in order to realise maximum membrane surface per volume). The extraction liquid thus flows down one side of the membrane (inner side of hollow fibre). The waste water is passed along the other side of the membrane (outer side of hollow fibre). The pores of the membrane are then filled with the organic extractant. The polluted substances diffuse from the waste water, through the membrane and to the extractant. The extractant can be regenerated using (amongst other things) a vacuum film vaporiser. It is possible to reuse the extractant.

Selectivity can be influenced by the choice of the extractant. In a number of cases, the distribution coefficients of the various pollutants to be removed do not or barely differ, whereby selective separation becomes difficult or expensive because multiple steps need to be implemented. However, in order to remove organic substances from water, for example, selective separation is generally not needed.

Applicability
The process has been demonstrated at pilot scale at various installations. A full-scale installation of 15 m^3/h has been operational at an industrial site in the Netherlands since 1998. The pertraction installation is equipped with membrane contactors containing polypropylene hollow fibres. It treats 15 m^3/h waste water originating from a chemical reactor containing aromatic compounds. In the pertraction installation the organic compounds are extracted from the waste water with a feedstock for the reactor as the extractant. In this way the water is not only cleaned but lost product is also recycled back to the reactor. Moreover, the existing waste water incineration installation was put out of operation thanks to the pertraction installation by which the company saves 5 million m^3 natural gas annually. The installation runs with a removal efficiency of at least 95 % for the aromatic compound [244, Klaassen et al. 2007] [245, Klaassen et al. 2005]. Pertraction modules (i.e. membranes) have, in the meantime, become commercially available. However, in 2011 the membrane stability could not be sufficiently guaranteed.

Advantages and disadvantages are given inTable 3.89.

Table 3.89: Advantages and disadvantages associated with pertraction

Advantages	Disadvantages
• Use of a much lower quantity of extractant and the ability to work without implementing an often time-consuming separation phase between waste water and extractant • Compact design • Relatively simple process • Low consumption of energy	• Membrane could become polluted if membrane-polluting compounds are present

Pertraction can be cost-effectively implemented for the removal of organic compounds from industrial process water, waste water or polluted groundwater.

The technique can be used for the removal of a broad spectrum of compounds. It is possible to effectively remove pollutants that are difficult to biodegrade, as well as pollutants that are easily biodegradable. Pertraction is especially suitable for the removal of hydrophobic organic compounds like aromatic and aliphatic organics, chlorinated solvents (e.g. carbon tetrachloride, chloroform, tetrachloroethene, trichloroethene), PCBs, di- and tri-chlorobenzene, pesticides and higher polycyclic hydrocarbons.

It is also possible to remove unwanted metal elements (amongst other things) from passivation baths in the galvanisation industry, using a specific form of pertraction, namely emulsion pertraction. The only difference with normal pertraction is that the watery extractant is dispersed in an organic liquid.

Economics

The cost of pertraction is to a great extent determined by the quantity and composition of the waste water flow to be treated and the effluent concentrations to be achieved. The quantity of extractant plays a major role during process optimisation. A larger quantity of extractant means a greater driving force and thus a smaller membrane surface. A smaller extractant quantity results in a smaller regeneration unit.

To provide an example, costs have been estimated for the treatment of waste water with trichloroethylene pollution. For a waste water flow volume of 10 m^3/h and a concentration of organic substances of 10 mg/l in the influent, the total cost (in 2005) using pertraction amounted to EUR 0.49 per m^3 of treated water to achieve a concentration in the water effluent of 10 µg/l. Whereas, for the same waste water, the total cost is estimated to be EUR 1.03 per m^3 of treated water with activated carbon filtration and EUR 0.67 per m^3 with air stripping (with air treatment) [244, Klaassen et al. 2007] [245, Klaassen et al. 2005]. This makes pertraction cheaper than air stripping followed by activated carbon filtration, or only activated carbon filtration with a configuration of two filters in series. Pertraction also applies to waste water volumes in the range of 1.5–100 m^3/h.

The situation is clearly different for biodegradable substances like toluene. In this case, pertraction is only more favourable than biological treatment or adsorption on activated carbon for low waste water volumes and high removal rates.

Driving force for implementation

Compared to conventional extraction, the main driving force for implementation of pertraction is the reduced use of extractant.

Example plants

Chemical firm KoSa Netherlands BV in Vlissingen, the Netherlands.

Sectors where pertraction is used include:

- the chemical, pharmaceutical and petrochemical industries;
- waste water treatment plants;
- surface treatment using organic solvents;
- the metal industry;
- tank cleaning;
- chemical laundries;
- wood conservation.

Reference literature

[63, VITO 2010] [244, Klaassen et al. 2007] [245, Klaassen et al. 2005]

3.3.2.3.4.14   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 substances that otherwise would be decomposed (if distillation occurred at higher temperatures).

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.

Achieved environmental benefits
Achieved environmental benefits associated with distillation/rectification are given in Table 3.90.

Table 3.90:   Abatement efficiencies and emission levels associated with distillation/rectification

Parameter	Abatement efficiency (%)	Emission level (mg/l)	Comments
Phenols	96	2 000	Feed 50 g/l
Methanol	97.5	2 000	Feed 80 g/l
Epichlorohydrin	90	700	Feed 7 g/l
Aniline	97.5	100	Feed 4 g/l
Chlorobenzene	90	10	Feed 100 mg/l
Source: [22, BMU/LAWA 2000].			

Distillation vents may give rise to VOC emissions and these can be treated, e.g. by incineration (see Section 3.5.1.3.5).

Cross-media effects
Distillation implies the consumption of energy.

Operational data
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.

Applicability
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 for the following reasons:

- 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 are given in Table 3.91.

Table 3.91: Application limits and restrictions associated with distillation/rectification

Issue	Limits/restrictions
Feed concentration	• Needs to be large enough for distillation to become economically feasible
Boiling temperature	• Substantial difference between boiling temperatures of waste water and contaminants • Azeotropic mixtures need auxiliaries, or distillative separation is not possible

Advantages and disadvantages are given in Table 3.92.

Table 3.92: Advantages and disadvantages associated with distillation/rectification

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

Economics
No information provided.

Driving force for implementation
The driving force for implementation is the recovery of materials (e.g. solvents) from waste water streams.

Example plants
Distillation/rectification is broadly used in the chemical industry, especially in the LVOC and OFC sectors.

For WWTP #16, the use of distillation was reported for the treatment of waste water streams from the production of pharmaceuticals [222, CWW TWG 2013].

Reference literature
[22, BMU/LAWA 2000] [222, CWW TWG 2013]

3.3.2.3.4.15   Evaporation

Description
Evaporation of waste water is a distillation process (see Section 3.3.2.3.4.14) 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 the 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 the fertiliser industry to concentrate urea, phosphoric acid, ammonium nitrate, etc.;
- agitated thin film evaporators, used for concentrating, fractionating, deodorising 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 operating conditions are 12–20 kPa and 50–60 °C.

Storage facilities have to be provided for residues before their disposal (or recycling).

Achieved environmental benefits
Water is evaporated. Depending on the influent and type of pollution, the effectiveness lies around 99 % [63, VITO 2010].

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 given in Table 3.93.

Table 3.93:   Consumables associated with evaporation

Consumable	Amount
Chemicals for pretreatment	NI
Steam (for heating)	5–16 kg water/kg steam
Energy (kWh/l)	Vacuum evaporation: 0.25–0.45 ([1])
([1]) [63, VITO 2010].	
NB: NI = no information provided.	

Operational data

Monitoring

Proper maintenance of the heat exchangers is crucial. 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.

Applicability

Evaporation is applied when concentrated waste water streams are wanted or recommended, in order to:

- concentrate mother liquors and liquors from waste gas scrubbing to recycle valuable substances;
- evaporate and crystallise solids, either to recover or remove them from the waste water effluent;
- pretreat the waste water stream by concentrating it 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 [22, BMU/LAWA 2000].

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 are given in Table 3.94.

Table 3.94:   Application limits and restrictions associated with evaporation

Issue	Limits/restrictions
Fouling	• Heat exchangers tend to foul
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 are given in Table 3.95.

Table 3.95: Advantages and disadvantages associated with evaporation

Advantages	Disadvantages
• Material recovery possible • Enables the 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

Economics
The costs are given in Table 3.96.

Table 3.96: Economics associated with evaporation

Type of costs	Costs	Comments
Investment costs	EUR 50 000 (Flow 70 l/h) EUR 155 000 (Flow 300 l/h) ([1])	Vacuum evaporation
Operating costs	NI	—
([1]) EUR 245 000 (Flow 300 l/h) in the case of a more corrosion-resistant stainless steel (i.e. AISI 316 – EURONORM X 6 CrNiMo 17 12 2). NB: NI = no information provided. *Source:* [63, VITO 2010].		

Driving force for implementation
The driving force for implementation is the recovery of materials from waste water streams and the minimisation of the waste water volume sent to treatment.

Example plants
Austin plant, Czech Republic [107, COM 2007].

Reference literature
[22, BMU/LAWA 2000] [63, VITO 2010] [107, COM 2007]

3.3.2.3.4.16   Pervaporation

Description
Pervaporation is a membrane process comparable to distillation. It combines permeation and vaporisation. Pervaporation employs both a concentration gradient and pressure as driving forces for separation. Volatile organic compounds are removed from a liquid feed solution through a semi-permeable membrane into the gas phase. The separation of the compounds from a liquid mixture is determined not only by differences in their vapour pressure but also by their permeation rates through the membrane. The driving force for permeation is the chemical potential difference of the compounds between the two phases separated by the membrane.

A vacuum is kept on the permeate side of the membrane while the feed side of the membrane is kept at atmospheric or elevated pressure so a pressure difference is created over the membrane which is the driving force for the pervaporation process. The compound(s) that permeates through the membrane evaporates while passing through the membrane because the partial pressure of the permeating compound(s) is kept lower than the equilibrium vapour pressure. In most cases, the permeate is recondensed.

A schematic of the technique is shown in Figure 3.34.

Source: [63, VITO 2010]
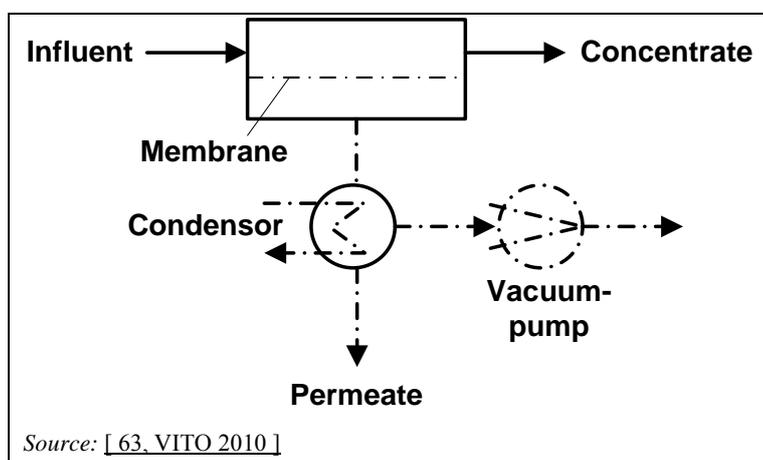
Figure 3.34: Pervaporation

There are different types of membranes for pervaporation: organic membranes, also called polymeric membranes, and inorganic membranes, also called ceramic membranes. A major drawback of polymeric membranes is their limited solvent and temperature stability. Generally, ceramic membranes are solvent and temperature stable, can be used in a broad pH range and have both high selectivity and permeability.

The pervaporation process, according to the widely accepted sorption-diffusion model, consists of three consecutive steps:

- specific sorption in the membrane layer of one or more compounds in the feed mixture depending on the characteristics of the membrane;
- diffusion of the compounds through the membrane;
- desorption of the compounds on the permeate-side as vapour.

Pervaporation is not based on a liquid/vapour balance like distillation, but is based on differences in sorption and diffusion of the various compounds in the feed. Thus, it is an interesting alternative for separating azeotropic mixes, which have the same composition in the vapour and the liquid phase, or mixes with similar boiling points. Furthermore, it offers an energy advantage because only the permeating compound must be converted into the gas phase.

There is also an alternative process, referred to as vapour permeation. Vapour permeation involves the feed being introduced in vapour form before it comes into contact with the membrane. This alternative is particularly interesting if the feed comes from an earlier process step in vapour form.

Achieved environmental benefits
In removal of volatile organic compounds (including chlorinated hydrocarbons and BTEX) from waste water, pervaporation is competitive with active carbon adsorption and stripping. Pervaporation easily removes compounds from water to levels below 1 %. Higher concentrate purification levels are possible but require a relatively large membrane surface, because the encountered fluxes are relatively low (low driving force) [63, VITO 2010].

Cross-media effects
The technique has the potential to save energy at a rate above 50 % compared to distillation. If the correct pretreatment is implemented (e.g. microfiltration) in the presence of suspended matter, and if a vapour permeation process is used for the presence of salts, then no problems are expected during membrane cleaning – thus no chemicals are needed.

Operational data
In order to have sufficient flux during pervaporation, work is normally carried out at temperatures between 50 °C and 100 °C. Typical fluxes averaged for a pervaporation process are around 1 kg/(m^2×h). Pervaporation is a relatively simple process. The parameters for process optimisation are temperature, vacuum, feed rate and feed concentration.

Applicability
Pervaporation/vapour permeation is a practical and financially viable alternative to distillation when draining solvents, particularly where azeotropes must be degraded or liquids with similar boiling points must be separated. In such cases, a hybrid process (distillation combined with pervaporation) is normally the most economically viable solution.

Hydrophilic pervaporation or vapour permeation can also be used to remove water from a reaction mixture and thus favourably alter the reaction balance. This is, for example, used for esterification reactions.

Pervaporation should be implemented to remove the minority compound(s) from a mixture. In this case, the required membrane surface and required energy will be at their lowest. Most pervaporation membranes work optimally when the permeating compounds in the feed are below a particular maximum level. Compounds with high boiling points make pervaporation more difficult. They restrict selectivity and can block the membrane.

Economics
A theoretical economic evaluation of a hybrid distillation/pervaporation unit for a to-be-processed isopropanol/water mix (50/50 wt-%) by Van Hoof et al. (2004) resulted in the following costs both with polymeric and ceramic membranes (lower costs with ceramic membranes):

- operating costs (primarily energy): ~ EUR 17/t product;
- investment costs: ~ EUR 40/t product;
- maintenance (including membrane replacement): ~ EUR 13/t product.

Thus the costs, for draining solvents that form an azeotrope, using such a hybrid distillation/pervaporation process, are around half of those associated with 'classic' azeotropic distillation.

Considering the limited implementation, no investment costs can be mentioned for a full-scale installation.

Driving force for implementation
The driving force for implementation compared to more classic technologies such as distillation is the significant energy savings.

Example plants
Throughout the world, there are various large-scale implementations, with the majority addressing drainage of alcohol (ethanol and isopropanol). The capacity of most installations lies between 50 l/d and 300 l/d. Thus, these are rather small installations.

Examples of sectors where pervaporation can be implemented are the chemical industry, the pharmaceutical industry, the petrochemical sector, refineries and paint, gloss, and varnish or printing-ink production.

Reference literature
[63, VITO 2010] [203, Van Hoof et al. 2004]

3.3.2.3.4.17   Stripping

Description

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 (e.g. ammonia, methanol) 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 reused. Volatile organic and inorganic compounds 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 exploiting waste heat. If there is no existing steam generation equipment, steam stripping might not be economically feasible.

The most common stripping facilities are as follows.

- Packed tower strippers, equipped with spray nozzles at the top to distribute waste water over the packing. The stripping gas is led countercurrent through the packing; a sump at the bottom collects the decontaminated water. Packed tower strippers are additionally equipped with an air heater (for air stripping), an automated control system and a control system for emissions to air (GAC unit, catalytic oxidiser or incinerator).
- Stripping tanks, 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 batch-wise.

The subsequent removal of the volatile pollutants from the gas phase can be accomplished by:

- adsorption on GAC, zeolite or synthetic resins (see Section 3.5.1.2.3);
- absorption by non-aqueous solvent and subsequent desorption (see Section 3.5.1.2.4);
- absorption by aqueous solutions, such as strong acids (to absorb ammonia, see Section 3.5.1.2.4);
- condensation or partial condensation and subsequent further treatment (see Section 3.5.1.2.2);
- thermal oxidation (see Section 3.5.1.3.5) or catalytic oxidation (see Section 3.5.1.3.6).

An example of a stripping process (i.e. the air/steam stripping of ammonia) is illustrated in Figure 3.35.
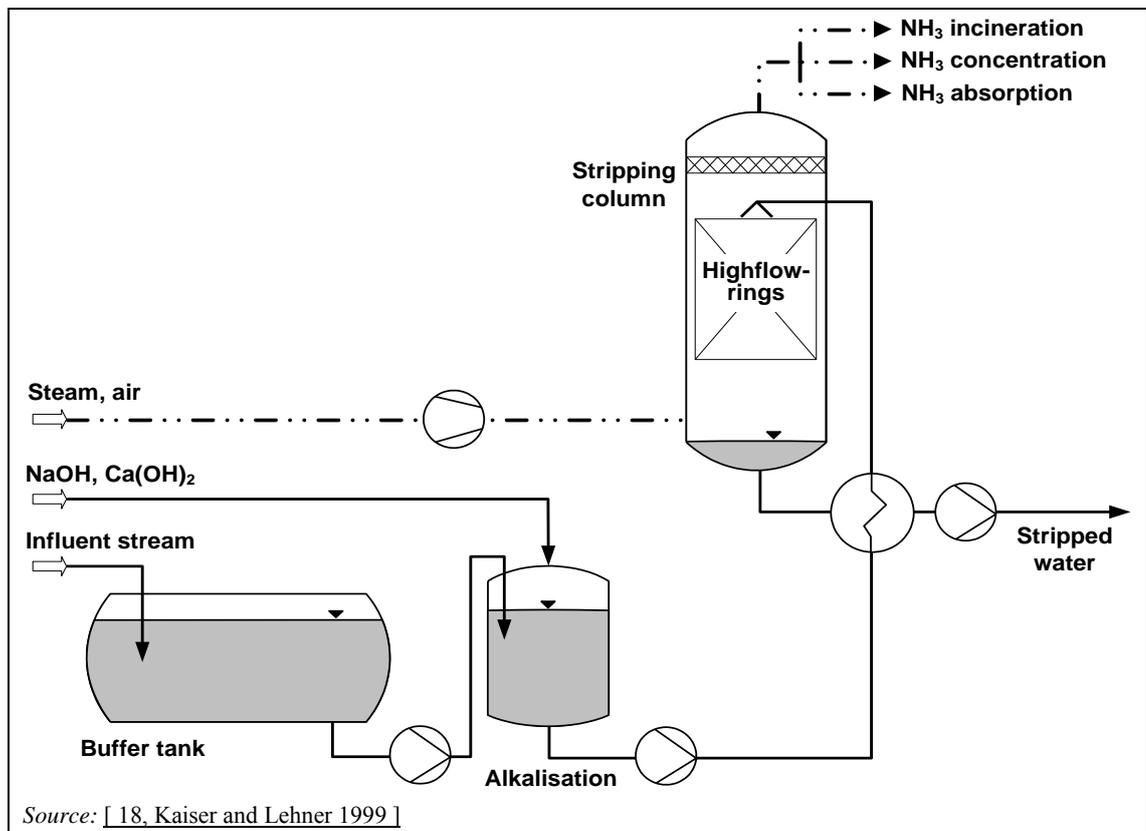
Figure 3.35: Air and steam stripping of ammonia

Achieved environmental benefits
Achieved environmental benefits associated with stripping are given in Table 3.97.

Table 3.97: Abatement efficiencies and emission levels associated with stripping

Pollutant	Abatement efficiency (%)		Emission level (mg/l)		Comments
	Air	Steam	Air	Steam	
Ammonia	NI	NI	< 5 ([1])	NI	Low feed concentrations and optimum conditions
	NI	99 ([2])	NI	< 50 ([2, 3])	Feed 10 g/l
	> 92 ([4, 5])	NI	70 ([4])	NI	Filtrate from the treatment of activated sludge, feed 500–1 200 mg/l, feed rate 19–24 m^3/h
VOCs	99 ([1])	NI	NI	NI	Feed rate 1 m^3/h, concentration 2 g/l (dichloromethane, trichloro-methane, benzene, toluene, xylene, esters, ethers)
Methanol	NI	97	NI	NI	Feed rate 3.4 m^3/h, concentration 36 g/l
Chloromethane	NI	NI	NI	< 1 ([1])	Feed rate 6 m^3/h, concentration > 200 mg/l
Dichloromethane	NI	99 ([1])	NI	NI	Feed rate 4 m^3/h, concentration 5 g/l
Tetrachloromethane	90–98 ([2])	NI	NI	NI	Packed tower, air/water 5/1 to 35/1
1,2-Dichloroethane	65 ([2])	NI	NI	NI	Packed tower, air/water 35/1
Trichloroethene	69–92 ([2])	NI	NI	NI	Packed tower, air/water 4/1 to 30/1
	90 ([2])	NI	NI	NI	Spray aeration
Perchloroethene	95 ([2])	NI	NI	NI	Packed tower, air/water 5/1
	90 ([2])	NI	NI	NI	Spray aeration
Methylal	NI	99 ([1])	NI	NI	Feed rate 4 m^3/h, concentration 30 g/l
BTEX	NI	> 99 ([1])	NI	NI	Feed 400 m^3/h, concentration 500–1 000 mg/l BTX
Phenols	NI	99–99.6 ([6])	NI	50–200 ([6])	Feed 7–8 m^3/h, concentration 20–40 g/l

([1]) [22, BMU/LAWA 2000].
([2]) [3, Environment Agency (England and Wales) 1997].
([3]) If caustic is added, emission levels of 10–15 mg/l can be achieved with sour water stripping using steam [227, CWW TWG 2009].
([4]) [73, Sackewitz 1999].
([5]) The performance of air stripping of ammonia is highly dependent on air temperature and air/water ratios. Efficiency decreases significantly as air temperature decreases. At 20 °C, there is a 90–95 % ammonia removal efficiency, while at 10 °C, efficiency decreases to 75 % [241, US EPA 2000].
([6]) [36, NOREC 2000].
NB: NI = no information provided.

Further performance data can be found in the OFC BREF [105, COM 2006].

Cross-media effects
Stripping is not used as an individual process. It needs at least downstream gas treatment. The removed VOCs are either recycled to a production process or treated (e.g. by 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 overall efficient treatment, 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 given in Table 3.98.

Table 3.98: Consumables associated with stripping

Consumable	Amount	
	Air stripping	**Steam stripping**
Chemicals to adjust pH (acid, caustic soda, lime)	Stoichiometric	Stoichiometric
Anti-fouling agents	NI	NI
Steam	NI	0.1–0.3 tonne/m^3 ([1, 2])
Energy (kWh/m^3)	0.1–0.2 (with biofilter as air treatment technique) ([3]) 0.3–0.5 (with activated carbon as air treatment technique) ([3])	680 ([4, 5])
Electrical	1.8 ([6, 7])	NI
Gas (heating) (m^3 gas/m^3 water)	0.5 ([6])	NI

([1]) [3, Environment Agency (England and Wales) 1997].
([2]) [22, BMU/LAWA 2000].
([3]) [63, VITO 2010].
([4]) [36, NOREC 2000].
([5]) Including steam generation.
([6]) [73, Sackewitz 1999].
([7]) Engine-driven equipment such as pumps and vents.
NB: NI = no information provided.

Operational data
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.

Applicability
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 is 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 [76, Ecker and Winter 2000];
- organic solvents, petrol, diesel fuel, low aromatics, phenol, mercaptans.

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 are given in Table 3.99.

Table 3.99: Application limits and restrictions associated with stripping

Issue	Limits/restrictions
Fouling	Heat exchangers tend to foul
Suspended solids	< 5 ppm

Advantages and disadvantages are given in Table 3.100.

Table 3.100: Advantages and disadvantages associated with stripping

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 and therefore injection of anti-fouling agents is necessary • Stripping gas should be treated • Frequent column cleaning required

Economics
Economics associated with astripping are given in Table 3.101.

Table 3.101: Economics associated with stripping

Type of costs	Costs (thousand) [1]		Comments
	Air	**Steam**	
Investment costs	GBP 70–100 (EUR 85–120)	GBP 200–300 (EUR 240–370)	Treatment of 50 m^3/h of waste water
Operating costs	GBP 15–20 (EUR 18–24)	GBP 300–400 (EUR 370–490)	
[1] Average currency conversion rate for 1996: EUR/GBP = 0.8188.			
Source: [32, ETBPP 1996].			

Operating costs for the combination of stripping and thermal oxidation are given in the OFC BREF [105, COM 2006].

Driving force for implementation
The main driving forces for implementation are to enable product recovery and to meet emission limit values.

Example plants
The technique is used in particular in the LVOC and OFC sectors [104, COM 2003] [105, COM 2006].
The use of stripping was reported for some WWTPs of the survey [222, CWW TWG 2013]:

- WWTP #01: pretreatment of waste water from the production of pharmaceuticals;
- WWTP #12: pretreatment of waste water streams with high concentrations of purgeable AOX and solvents from an OFC site;
- WWTP #19: pretreatment of waste water for the removal of dichloromethane.

Reference literature
[3, Environment Agency (England and Wales) 1997] [18, Kaiser and Lehner 1999] [22, BMU/LAWA 2000] [32, ETBPP 1996] [36, NOREC 2000] [63, VITO 2010] [73, Sackewitz 1999] [76, Ecker and Winter 2000] [104, COM 2003] [105, COM 2006] [222, CWW TWG 2013] [227, CWW TWG 2009] [241, US EPA 2000]

3.3.2.3.4.18   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 ºC and 1 200 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/incineration 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. This section provides an overview of waste water incineration in the chemical industry sector. More general information on waste incineration can be found in the Waste Incineration BREF [108, COM 2006].

The combined incineration of liquid and waste gases is dealt with in a summarised way in Section 3.5.3 (for more information, see the Waste Incineration BREF [108, COM 2006]).

Waste water incineration is only self-sustaining if the organic load is sufficient to ensure adequate energy support for the 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 3.3.2.3.4.15), 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 [251, Ullmann's 2000].

Devices for waste water incineration can be constructed as ordinary combustion chambers or fluidised-bed incinerators. There is a high demand for 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.

Incineration is often the treatment of choice to treat waste waters from chemical multi-product plants with diverse toxic or very toxic waste water streams, which cannot be routed to a conventional waste water treatment plant.

Because there is a risk of dioxin/furan (PCDD/PCDF) formation when chlorinated compounds are incinerated, the following operating conditions are generally considered appropiate for the

incineration of halogenated organic substances (these conditions are indicated in Chapter IV of Directive 2010/75/EU on industrial emissions [5, Directive 2010/75/EU 2010]):

- temperature $> 1\,100\,°C$ (850 °C when incinerating waste with less than 1 % of halogenated, organic substances);
- residence time > 2 s;
- oxygen content > 3 %.

In addition, conditions that favour formation of dioxins/furans immediately following combustion are to be prevented. This is achieved by a 'fast quench' of post-combustion gases by cooling them very quickly from high temperatures to below the temperature window of dioxins/furans' reformation.

These measures are designed to keep PCDD/PCDF emissions below $0.1\,\text{ng TEQ/Nm}^3$. In the case of the combustion of halogenated VOC substances, an HCl scrubber is necessary.

Achieved environmental benefits
Achieved environmental benefits associated with waste water incineration are given in Table 3.102.

Table 3.102: Abatement efficiencies and emission levels associated with waste water incineration

Pollutant	Abatement efficiency (%)	Emission level (mg/l)	Comments
TOC	> 99	NI	—
NB: NI = no information provided.			
Source: [22, BMU/LAWA 2000].			

The achievable emission levels and abatement efficiencies in Table 3.102 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 flue-gases are regulated by the Directive 2010/75/EU on Industrial Emissions, in particular by its Chapter IV and Annex VI [5, Directive 2010/75/EU 2010]. Further information can be found in the BREF on Waste Incineration [108, COM 2006].

Cross-media effects
Waste water incineration results in flue-gas (potentially containing HCl, SO_X, NO_X, etc.) which, depending on its content, may need further treatment resulting in additional waste water and solid waste. When the process cannot be operated autothermally, supporting fuel is required. Meanwhile, when the waste heat cannot be recovered or reused, some heat is released into the environment.

Consumables are given in Table 3.103.

Table 3.103: Consumables associated with waste water incineration

Consumable	Amount
Supporting fuel (low TOC content)	NI
Electric energy for pumps, burners, etc. (kWh/m^3)	NI
NB: NI = no information provided.	

Operational data

Monitoring

Throughout the process, thorough monitoring of operating parameters is needed, such as oxygen content, temperature, content of sulphur oxides, nitrogen oxides, hydrogen halides, and dust, to ensure faultless working.

Applicability

Incineration is applied to waste water which contains 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 include:

- aqueous residues from dye production;
- aqueous residues from rubber production, containing extremely large loads of salt;
- aqueous extracts from pesticide production;
- 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 [251, Ullmann's 2000]:

- the organic constituents cannot be reused 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 for incineration generally cover a range between 2 m^3/h and 30 m^3/h with COD concentrations between 50 000 mg/l and 100 000 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 are given in Table 3.104.

Table 3.104: Application limits and restrictions associated with waste water incineration

Issue	Limits/restrictions
Halogens and 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 are given in Table 3.105.

Table 3.105: Advantages and disadvantages associated with waste water incineration

Advantages	Disadvantages
• High organic content will be nearly completely removed • Elimination of pollutants also possible with a high salt concentration • Waste heat can be used	• Low organic concentrations need supporting fuel • Solid waste (bottom and fly ashes) need to be disposed of • Incineration of sulphur and/or halogenated compounds might demand flue-gas treatment, causing waste water and solid waste

Economics
No information provided.

Driving force for implementation
The driving force for implementing the technique is to relieve the biological treatment stage of particular COD/AOX loads with low biodegradability or inhibiting/toxic effects.

Example plants
Waste water incineration is used broadly in Europe (e.g. in the OFC sector).

Reference literature
[5, Directive 2010/75/EU 2010] [22, BMU/LAWA 2000] [108, COM 2006] [190, UBA DE 2009] [191, UBA DE 2009] [251, Ullmann's 2000]

3.3.2.3.5 Soluble biodegradable contaminants/biological treatment

3.3.2.3.5.1 Overview

The main production line in the chemical industry is the production and handling of organic substances. Thus most 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 before biological treatment (see Section 3.3.2.3.4).

Biological treatment is the degradation of dissolved organic substances with microorganisms (i.e. bacteria) as oxidising agents. Organic nitrogen and phosphorus 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 non-degradable waste water
- BOD/COD 0.2–0.4 moderately to highly degradable
- BOD/COD > 0.4 highly 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 an oxygen supply.

The main properties of these three metabolic processes in connection with waste water treatment are given in Table 3.106 [251, Ullmann's 2000].

Table 3.106: Specific process parameters normally associated with anaerobic, anoxic and aerobic biology

Parameter	Anaerobic	Anoxic	Aerobic
Dissolved oxygen (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 % ([1])	Varying, depending on denitrification	> 85 %
Nitrogen removal efficiency	0	45–90 % (nitrification required as first stage)	Moderate (assimilation of N to biomass)
Suitability as pretreatment	Yes	Yes	Yes
Suitability for last stage treatment	No	No	Yes
([1]) Normal value, can be higher for special applications (see Section 3.3.2.3.5.2, achievable emission levels/abatement efficiencies).			

A comparison of the carbon balance of aerobic and anaerobic processes is illustrated in Figure 3.36.

Source: [251, Ullmann's 2000]
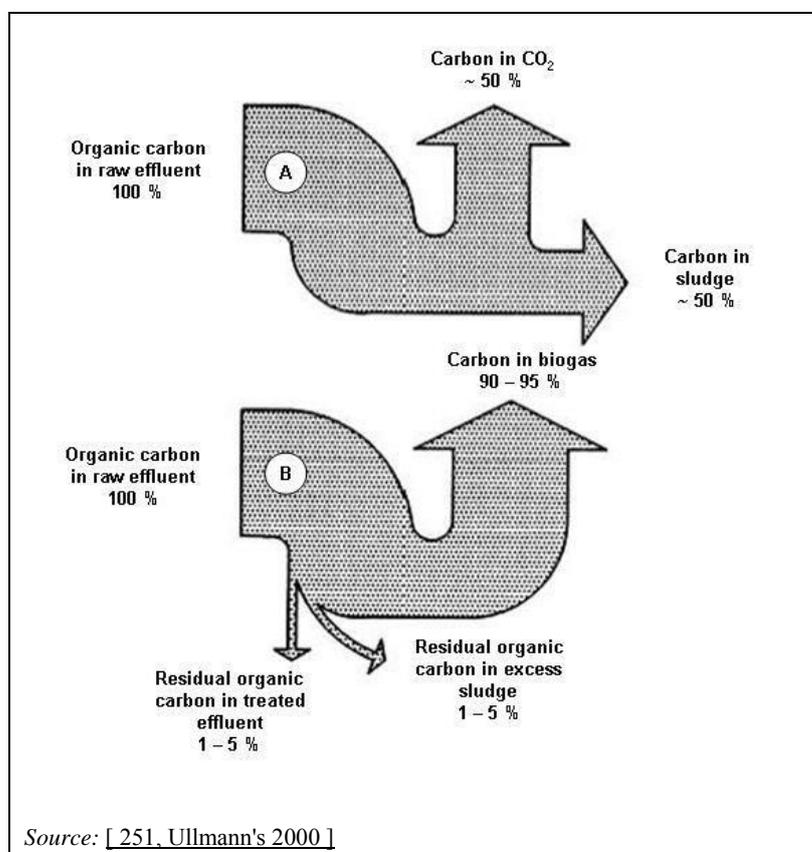
Figure 3.36: Carbon balances in the aerobic (A) and anaerobic (B) microbiological degradation of organic compounds

One advantage of biological waste water treatment – independent of the kind of metabolic process – is the relatively rapid adaptability of microorganisms to a wide variety of nutrient media.

Biological treatment techniques commonly used in the chemical industry are dealt with in the following sections.

3.3.2.3.5.2   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 (examples of biogas compositions are given in [63, VITO 2010]). The process is carried out in an airtight stirred tank reactor, and the microorganisms are retained in the tank as biomass (sludge).

There are several reactor types available. The most commonly used are:

- anaerobic contact reactor;
- upflow anaerobic sludge blanket (UASB) reactor;
- fixed-bed reactor;
- expanded-bed reactor.

In the **anaerobic contact process**, waste water is mixed with recycled sludge and digested in a sealed reactor, the waste water/sludge mixture is externally separated (e.g. by sedimentation, see Section 3.3.2.3.3.4, or using vacuum flotation, see Section 3.3.2.3.3.5) and the supernatant is discharged for further downstream treatment. The anaerobic sludge is recycled to the reactor [1, Metcalf and Eddy 1991].

In the **UASB process,** waste water is introduced at the bottom of the reactor 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 [1, Metcalf and Eddy 1991]. The principle is illustrated in Figure 3.37.

Source: [251, Ullmann's 2000]
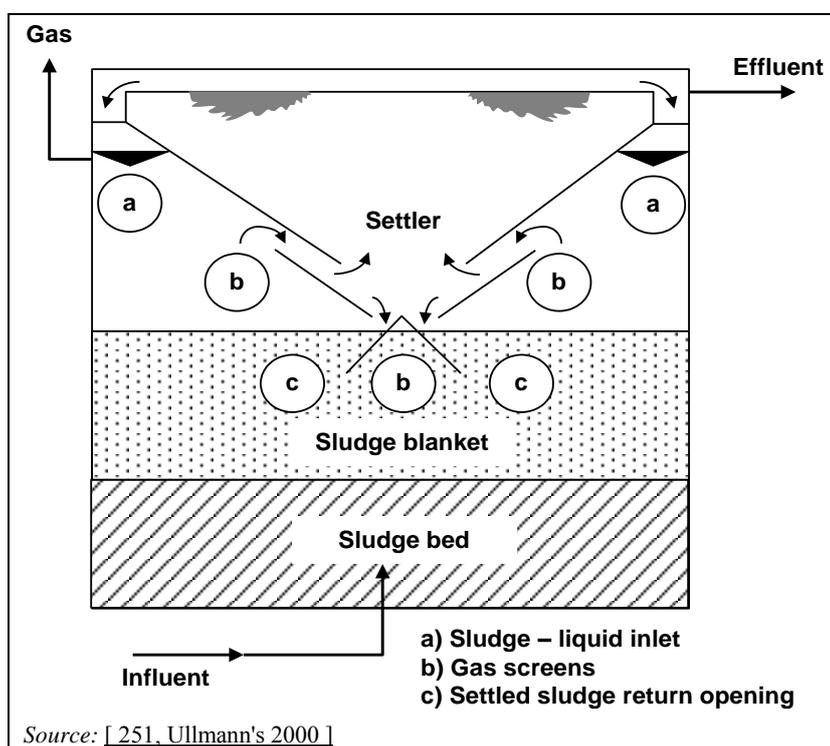
Figure 3.37: UASB process

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 microorganisms grow and are retained [1, Metcalf and Eddy 1991].
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 [1, Metcalf and Eddy 1991].

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 3.38.

Source: [251, Ullmann's 2000].
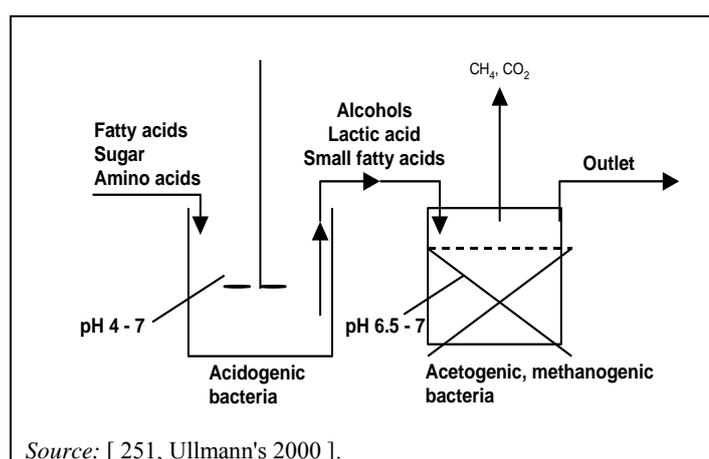
Figure 3.38: Two-stage anaerobic treatment process

Achieved environmental benefits
Achieved environmental benefits associated with anaerobic treatment are given in Table 3.107.

Table 3.107: Abatement efficiencies associated with anaerobic treatment

Process	Input COD (g/l)	Retention time (h)	Organic loading (kg/(m³×d))	COD removal (%)
Anaerobic contact process	1.5–5	2–10	0.48–2.40	75–90
UASB	5–15	4–12	4.00–12.0	75–85
Fixed-bed	10–20	24–48	0.96–4.81	75–85
Expanded-bed	5–10	5–10	4.81–9.62	80–85
Source: [1, Metcalf and Eddy 1991].				

The 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 non-degradable waste water streams as far as possible.

In combination with downstream aerobic treatment the total abatement efficiencies are given in Table 3.108.

Table 3.108: Abatement efficiencies associated with anaerobic treatment in combination with downstream aerobic treatment

Pollutant	Abatement efficiency (%)
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 1/1 to 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.

Operational data

Monitoring

Monitoring of a biological WWTP is illustrated in Section 3.2.2.1.

Applicability

Anaerobic waste water treatment is essentially used only as a pretreatment for waste water which is characterised by a high organic load (> 2 g/l) and a more or less constant quality [251, Ullmann's 2000]. 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 [251, Ullmann's 2000].

Application limits and restrictions are given in Table 3.109.

Table 3.109: Application limits and restrictions associated with anaerobic treatment

Issue	Limits/restrictions
Temperature	20–40 °C
pH	6.5–7.5, pH > 8 stops methane-forming process
Toxic substances	Introduction of toxic substances needs to be prevented, because the process is sensitive

Advantages and disadvantages are given in Table 3.110.

Table 3.110: Advantages and disadvantages associated with anaerobic treatment

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 • Low amount of clarification sludge (compared to the aerobic process – one tenth of it) (see Figure 3.36) • 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 is possible • Very slow start-up • Abatement efficiency not sufficient for final treatment stage (COD removal is normally < 85 %), thus requiring further treatment

Economics
Economics associated with anaerobic treatment are given in Table 3.111.

Table 3.111: Economics associated with anaerobic treatment

Type of costs	Costs	Comments
Investment costs	EUR 1 000 000 ([1])	UASB reactor (volume: 500 m^3, industrial waste water with a COD concentration of 3 000 mg/l, volumetric load: 5 kg COD/($m^3 \times$d))
Operating costs	NLG 0.3/m^3 (EUR 0.14/m^3) (NLG 20 000/yr (EUR 9 070/yr)) ([2])	206 m^3/d, raw COD load 7 300 kg/d or 35 g/l
Benefit (biogas)	NLG 210 000/yr (EUR 95 300/yr) ([2])	206 m^3/d, raw COD load 7 300 kg/d or 35 g/l
	NLG 1.5 million/yr (EUR 0.68 million/yr) ([2])	Compared to incineration of excess sludge
([1]) [63, VITO 2010]. ([2]) [38, Biothane 2000]. Fixed currency conversion rate from January 1999 onwards: EUR/NLG = 2.204.		

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).

Driving force for implementation
The driving force for implementation is to pretreat waste waters with high COD/BOD loads before aerobic treatment.

Example plants
Anaerobic treatment is used in the chemical industry sector, e.g. in Germany.

Reference literature
[1, Metcalf and Eddy 1991] [38, Biothane 2000] [63, VITO 2010] [251, Ullmann's 2000]

3.3.2.3.5.3   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 3.39.
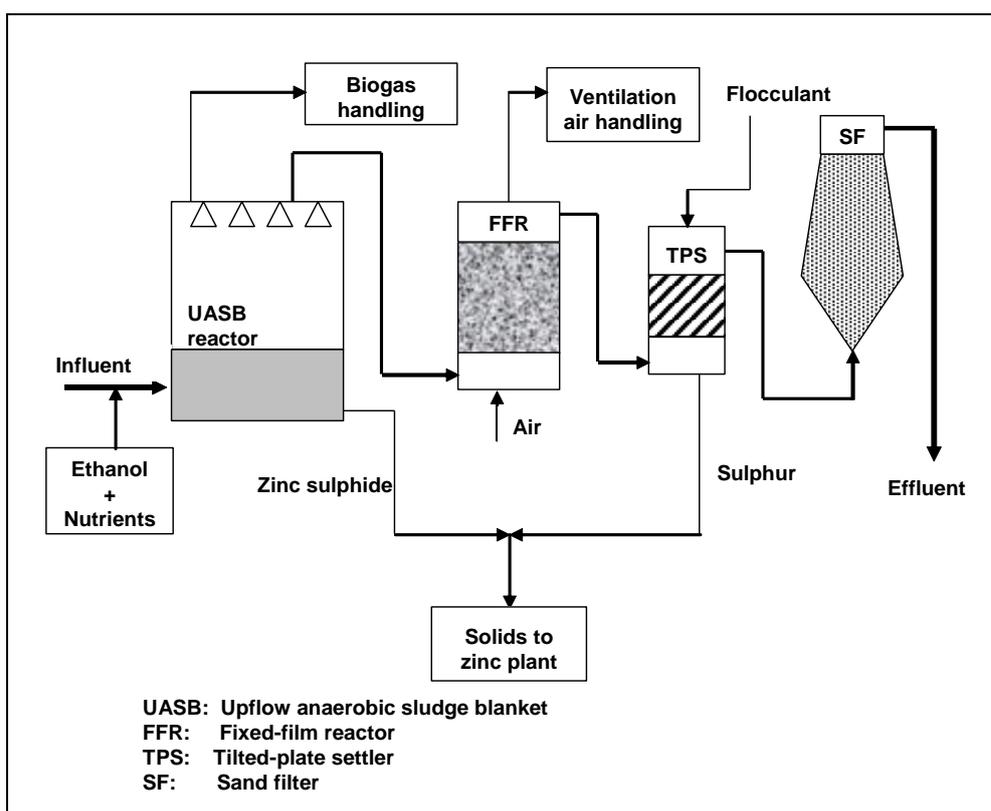
Figure 3.39: Process diagram of a biological metal and sulphate reducing plant

The main components of biological removal of sulphur compounds/heavy metals are:

- the UASB reactor, where the biological reduction of sulphate into sulphide takes place;
- the biogas handling system to use or control the waste gas originating from the UASB;
- the fixed-film reactor, where sulphide is aerobically converted into sulphur, and the bacteria is 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, for example:

- 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, part of the waste water after the tilted-plate settler or the sand filter can be recirculated, since the conversion of sulphide into sulphur increases the alkalinity.

The handling of biogas from the UASB reactor and of ventilation air from the fixed-film reactor enable odourless operation.

Achieved environmental benefits
Achieved environmental benefits associated with biological removal of sulphur compounds/heavy metals are given in Table 3.112.

Table 3.112: Abatement efficiencies and emission levels associated with biological removal of sulphur compounds/heavy metals

Pollutant	Abatement efficiency (%)	Emission level (mg/l)	Comments
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 1 170 mg/l, presence of heavy metals
([1]) [40, de Vegt and Buisman 1996]. ([2]) [39, Buisman 1991].			

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 reused to recover the metal. The sulphur fraction, when recovered separately, is produced as a sulphur cake, consisting of 60 % dry matter with a purity of 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 biogas 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.

Biological removal of sulphur compounds/heavy metals implies the consumption of energy, but may also imply the consumption of neutralising agents, electron donors, or flocculants.

Operational data
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.

Applicability
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 given in Table 3.113.

Table 3.113: Application limits and restrictions associated with biological removal of sulphur compounds/heavy metals

Issue	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 a stable operation
([1]) [39, Buisman 1991].	

Advantages and disadvantages are given in Table 3.114.

Table 3.114: Advantages and disadvantages associated with biological removal of sulphur compounds/heavy metals

Advantages	Disadvantages
• Treatment of sulphate without the addition of precipitant chemicals • Simultaneous removal of heavy metals and sulphate is possible • Heavy metals are separated from waste water as sulphides that may be reused • 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 a starting material in production processes (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 efficiency	• Often additional COD content is necessary such as an electron donor, which increases the operating costs • Metal sulphides mix with the biological sludge in the UASB reactor • Removal of heavy metals without sulphate is not possible

Economics
No information provided.

Driving force for implementation
The driving force for implementation is to comply with legislation on the quality of receiving water and to recover materials for reuse.

Example plants
Lenzing and Glanzstoff chemical plant producing viscose fibres in Austria, see POL BREF [106, COM 2007].

Reference literature
[39, Buisman 1991] [40, de Vegt and Buisman 1996] [106, COM 2007]

3.3.2.3.5.4   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 compounds are converted (mineralised) into carbon dioxide, water or other metabolites and biomass (i.e. the activated sludge).

Toxic waste water content can inhibit the biological process. Representative reported data with respect to threshold concentrations for detectable damage to activated sludge are given in Table 3.115. However, the acclimation of the bacterial community is an important factor and can affect the threshold inhibiting concentration.

Table 3.115: Threshold concentration of representative substances toxic to activated sludge

Substance	Inhibiting concentration (mg/l)
Cadmium (Cd^{2+})	2–5
Chromate (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	200–1 000
Hydrogen sulphide/Sulphide	5–30
Source: [251, Ullmann's 2000]	

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 microorganisms displaying increased resistance and a higher degradation potential [251, Ullmann's 2000].

Common aerobic biological treatment techniques are:

- complete mix activated sludge process;
- membrane bioreactor process;
- trickling or percolating filter process;
- the expanded-bed process;
- fixed-bed biofilter 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 (see also Section 3.3.3.1). The microorganisms are maintained as suspension in the waste water and the whole mixture is mechanically aerated. The activated sludge mixture is sent to a separation facility from which the sludge is recycled to the aeration tank. The separation facility can be:

- a sedimentation or settling tank (see Section 3.3.2.3.3.4);
- an air flotation facility (see Section 3.3.2.3.3.5);
- a MF or UF membrane (see Section 3.3.2.3.3.7; for a 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 requirements for emissions to air, etc. Examples of variants are:

- the oxidant agent: air or pure oxygen, the latter having the advantage of fewer 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 3.40;
- 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.

Source: [251, Ullmann's 2000]
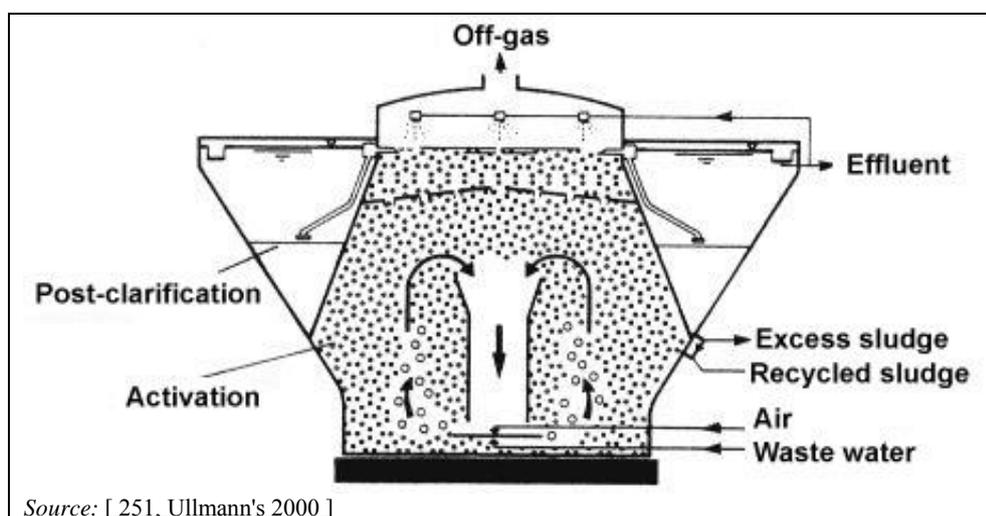
Figure 3.40: Example of tower biology

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 (see in particular Section 3.3.3.2). The different variations of this process are:

- an external recirculation loop between the activated sludge tank and the membrane module;
- immersion of the membrane module into 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 results in more compact plants.

These variants together with the conventional, activated sludge process are shown in Figure 3.41.

Fouling, as a major problem for membranes, is diminished by aeration and 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 approximately in the range of 5–15 g/l) [227, CWW TWG 2009] [242, VEOLIA 2010] [243, SIEMENS 2007];
- high sludge age (or mean cell residence time).

A membrane bioreactor is a compact facility (up to five 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, the energy consumption, because of pumping, may be significantly higher than with a conventional activated sludge process. Consumption of chemicals for cleaning membranes as well as membrane replacement result in higher operating costs for membrane bioreactors compared to conventional activated sludge systems.

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 3.42.

The liquid is collected in an underdrain system and passes 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 3.3.2.3.5.2) 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.

Source: Adapted from [90, INERIS 2001].
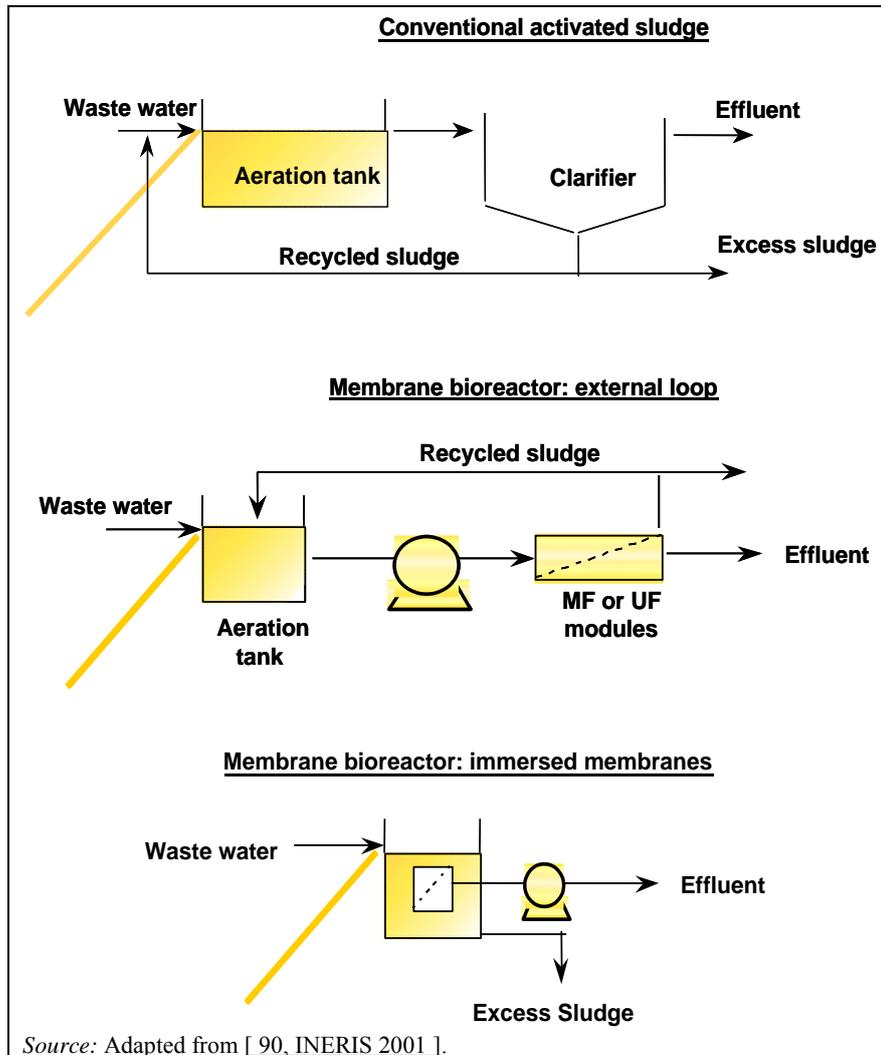
Figure 3.41: Variants of membrane bioreactor, compared with conventional activated sludge process
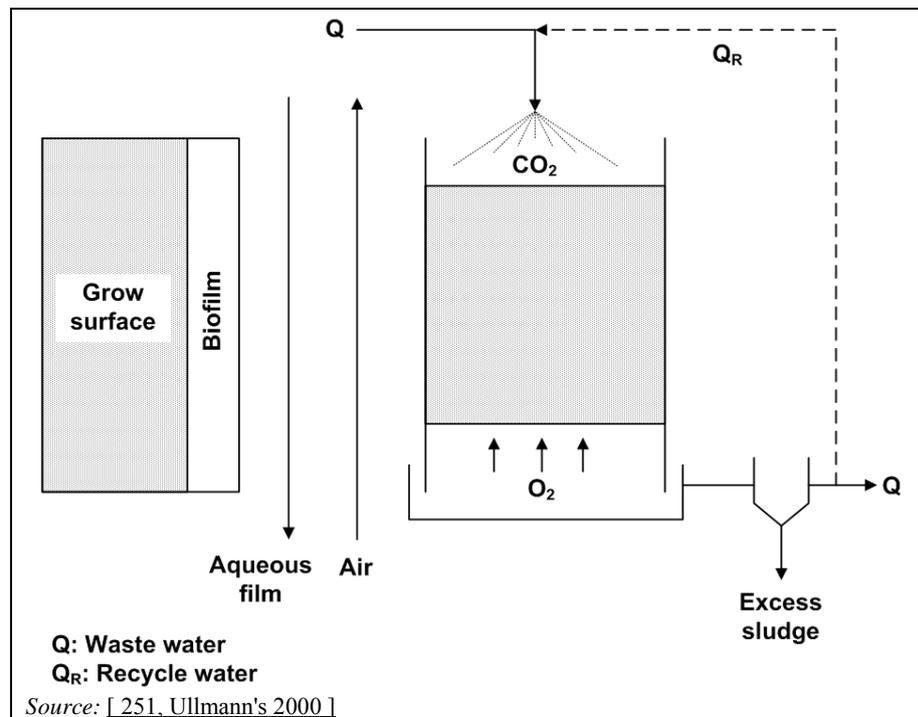
Figure 3.42: Trickling filter

In the **fixed-bed biofilter 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 3.43).
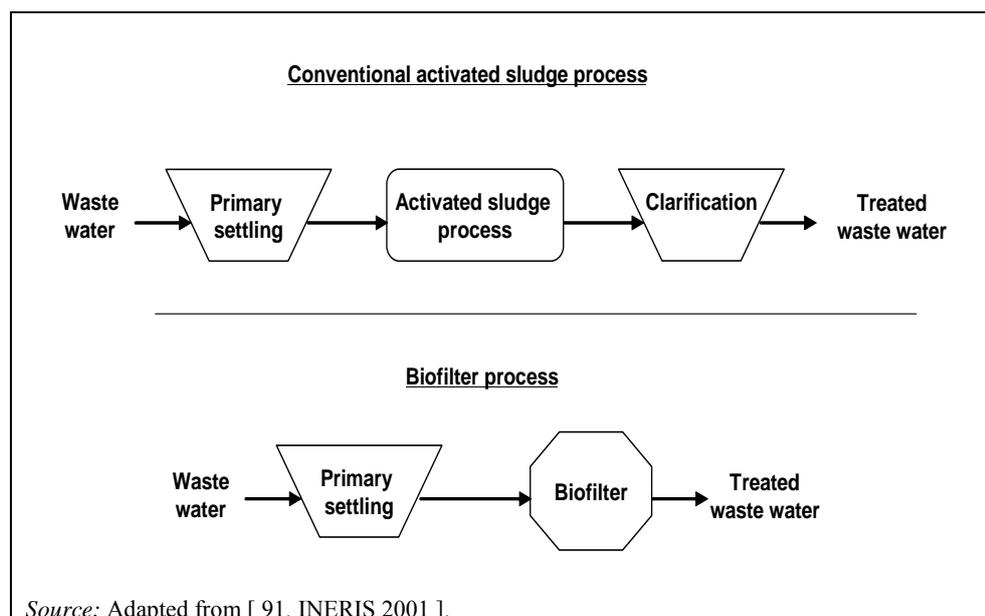
Figure 3.43: Biofilter process in comparison to conventional activated sludge process

Most submerged biofilters are based on one single filter medium. The water flow in a filter is upflow or downflow and with either a sinking or floating medium. Biofilters can have monolayer or multilayer construction. Multilayer biofilters are fed with raw water without

primary settling, whereas 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,
- both 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 beyond the normal residence time. Thus, refractory COD is more reduced than in a complete mix activated sludge process, as a 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.

Achieved environmental benefits

The main parameter to check the performance of biological treatment is BOD, while the degradation of COD depends on the degree of upstream pretreatment and the content of poorly 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 of a biological WWTP, it makes sense to list achievable COD levels.

Abatement efficiencies associated with aerobic treatment are given in Table 3.116. Some of the reported values are theoretical abatement efficiency values.

Table 3.116: Abatement efficiencies associated with aerobic treatment

Parameter	Abatement efficiency (%)				
	Complete mix activated sludge	Membrane bioreactor	Trickling filter	Expanded-bed	Fixed-bed biofilter
TSS	NI	99 ([1])	NI	NI	NI
Turbidity	NI	99 ([1])	NI	NI	NI
BOD	97–99.5 ([2])	97 ([1])	40–90 ([3]) 85–95 ([3, 4])	> 98 ([2])	NI
COD (TOC)	90–98 ([5])	> 90–96 ([1])	NI	90 ([2, 6])	26–68 ([7, 8])
Phenol index	> 99 ([9, 10])	NI	NI	NI	75–98 ([8])
AOX	NI	NI	NI	NI	55–98 ([8])
Total inorganic N	NI	82 ([1])	NI	NI	4–50 ([8])
NH$_4$-N	NI	96–98 ([1])	NI	NI	NI

([1]) [90, INERIS 2001].
([2]) [251, Ullmann's 2000].
([3]) [1, Metcalf and Eddy 1991].
([4]) Two-stage.
([5]) [222, CWW TWG 2013].
([6]) Three bioreactors in series, subsequent GAC adsorption results in TOC reduction of 98 %, COD reduction of 99 %.
([7]) Degradation of refractory COD, plant operates as polisher after activated sludge WWTP.
([8]) [78, Karl 2000].
([9]) Input phenol 30 mg/l, 2 200 m^3/d waste water.
([10]) [36, NOREC 2000].
NB: NI = no information provided.

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 rise to odour. This impact can be controlled by various means including the following.

- Replacement of air by pure oxygen or oxygen-enriched air. This has a number of advantages including reducing energy consumption, foam-forming and odour problems [63, VITO 2010] Odour is reduced due to the fact that the gas injection is reduced to about 20 % of the necessary air injection and hence there is a reduction of the stripping effect; the advantages of this process variant, however, need to be assessed carefully and balanced against the drawbacks, in particular those associated 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 sending the captured exhaust air to a downstream abatement system (such as a 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) serving as a 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 or off site, which are detailed in Section 3.4.2.

Consumables are given in Table 3.117.

Table 3.117: Consumables associated with aerobic treatment

Consumable	Complete mix activated sludge	Membrane bioreactor	Trickling Filter	Expanded-bed	Fixed-bed biofilter
Oxygen (air or pure gas)	NI	NI	NI	NI	NI
Neutralisation chemicals	NI	NI	NI	NI	NI
Flocculants	300–550 kg/t COD [1, 2]	NI	NI	NI	NI
Nutrients	23–42 kg/t COD [2, 3]	NI	NI	NI	NI
Carrier	NI	NI	NI	NI	NI
Energy (kWh/m^3)	9.5 [2, 4] 0.1 kWh per p.e. [5]	[6]	NI	NI	NI

[1] Flocculant: ferrosulphate.
[2] [36, NOREC 2000].
[3] *o*-Phosphoric acid.
[4] Including sludge incineration.
[5] [63, VITO 2010].
[6] MBRs use more energy than conventional processes in order to move water through the membrane and for membrane scouring and cleaning. The energy requirements of MBR systems may be twice those of conventional activated sludge systems [166, US EPA 2010] [171, WEF 2009].

NB: NI = no information provided.

Operational data

<u>Monitoring</u>
Monitoring of a biological WWTP is illustrated in Section 3.2.2.1.

Applicability
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 compounds 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 a 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 (because the resultant small space footprint of a membrane bioreactor enables the entire process to be housed);
- 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 two to three times higher than a high-loaded activated sludge plant and still remove 90 % of the COD [91, INERIS 2001]. A comparison of the loads treated by different biosystems is shown in Table 3.118 [91, INERIS 2001]. Biofiltration achieves the same performance with nitrification/denitrification, but with a higher load.

Table 3.118: Comparison of the volumetric loads treated by various aerobic processes

Treatment system	COD (kg/(m³/d))	BOD (kg/(m³/d))	NH₄-N (kg/(m³/d))	NO₃-N (kg/(m³/d))
Activated sludge	0.4–6	0.35–3 [1]	0.04–0.1	0.24–0.72
Activated sludge with oxygen-enriched aeration	NI	2–5 [2]	NI	NI
Biofilter	3–25	1.3–10 [1]	0.4–1.5	0.7–6
Trickling filter (with plastic support)	NI	1–5 [2]	NI	NI
Membrane bioreactor	2–3 [3, 4]	NI	0.9 [4, 5]	NI

[1] BOD_5.
[2] BOD_7.
[3] Peaks between 1.6 and 8.5 kg $COD/(m^3/d)$.
[4] [90, INERIS 2001].
[5] From thermal treatment liquor.

NB: NI = no information provided.

Application limits and restrictions are given in Table 3.119.

Table 3.119: Application limits and restrictions associated with aerobic treatment

Issue	Limits/restrictions
Nutrients	BOD/N/P should be 100/5/1; critical ratios that should not be exceeded to ensure adequate operation are 32/1 for BOD/N and 150/1 for BOD/P
Concentration	High substance concentrations (even of non-toxic substances) need to be avoided
Inhibitors	See Table 3.115
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 microorganisms; fixed-film techniques are less vulnerable

Advantages and disadvantages are given in Table 3.120.

Table 3.120: Advantages and disadvantages associated with aerobic treatment

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 microorganisms with air and water) • Degradation mainly into harmless compounds	• High energy consumption required 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 of 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, the fouling of membranes can be a problem • High pressure drop, which leads to an increase in electric energy consumption • With activated sludge, the sludge carry-over in the case of poor sludge-settling quality characteristics can be a problem

Economics

Economics associated with aerobic treatment are given in Table 3.121.

Table 3.121: Economics associated with aerobic treatment

Treatment system	Investment costs	Operating costs
Complete mix activated sludge	EUR 18 million ([1])	About 2 % of investment costs ([2])
		FIM 0.60/m^3 (EUR 0.10/m^3) ([3])
	EUR 950 000 ([4])	About 2 % of investment costs ([4])
Sequencing Batch Reactor	EUR 250 000 ([5])	NI
Membrane bioreactor	EUR 16 million ([6]) (EUR 1 800/(m^3/d))	EUR 0.3/m^3 ([6])
	EUR 3 million ([7])	EUR 0.2–0.5/m^3 ([7])
	EUR 1 070/(m^3/d) for ~ 15 100 m^3/d plant ([8]) EUR 570/(m^3/d) for ~ 45 400 m^3/d plant ([8])	EUR 0.24/m^3 ([8])
Trickling filter	NI	NI
Expanded-bed	NI	NI
Fixed-bed biofilter	NI	< DEM 0.2/m^3 (< EUR 0.1/m^3) ([9])

([1]) 450 m^3/h, new central WWTP (1 aerated basin and 2 clarifiers) started in 2009 [227, CWW TWG 2009].
([2]) [63, VITO 2010].
([3]) About 90 m^3/h, COD 500–900 mg/l [36, NOREC 2000]. Fixed currency conversion rate from January 1999 onwards: EUR/FIM = 5.946.
([4]) Industrial waste water treatment, flow rate of 1 600 m^3/d, influent COD concentration 1 500 mg/l, investment costs include sludge storage, cost of labour: 1 day per week (installations < 1 000 p.e.), 2 days per week (installations < 4 000 p.e.), more than 3 days per week (installations > 5 000 p.e.) [63, VITO 2010].
([5]) Industrial waste water treatment, flow rate of 30 m^3/d, influent COD concentration 5 000 mg/l, investment costs include 100 m^3 buffer basin [63, VITO 2010].
([6]) Municipal waste water treatment, 50 000 p.e., about 10 000 m^3/d (400 m^3/h), operating costs include energy and chemical consumption, membrane cleaning, sludge removal and maintenance [63, VITO 2010].
([7]) Chemical industry, flow rate of 2 000 m^3/d, influent COD 3 000 mg/l [63, VITO 2010].
([8]) Investment costs vary with the size of the plant as the economy of scale applies: USD 6 million/MGD (EUR 4.0 million/MGD) for a 4 MGD plant and USD 3.2 million/MGD (EUR 2.2 million/MGD) for a 12 MGD plant. Operating costs are mainly attributed to power due to high mixed liquor concentration in the reactor and membrane cleaning costs: USD 1.23/1 000 gal (EUR 0.829/1 000 gal) [231, US EPA 2008]. Average currency conversion rate for 2008: EUR/USD = 1.483.
([9]) [78, Karl 2000]. Fixed currency conversion rate from January 1999 onwards: EUR/DEM = 1.956.
NB: MGD = million gallons per day; NI = no information provided.

Investment and operating costs are highly dependent on hydraulic and contaminant load, necessary implemented facilities such as API separator, neutralisation step, sludge separation equipment, etc. Thus cost information needs further refining in light of the equipment and load of the plant in question.

Driving force for implementation
The technique is used to comply with waste water legislation and to reduce waste water charges/fees.

Example plants
Aerobic treatment, and particularly the complete mix activated sludge process, is used in hundreds of installations in Europe and worldwide in the chemical industry sectors as well as in other sectors.

A membrane bioreactor process is used in Süd-Chemie in Germany (see Section 3.3.3.2).

Reference literature
[1, Metcalf and Eddy 1991] [36, NOREC 2000] [63, VITO 2010] [78, Karl 2000] [90, INERIS 2001] [91, INERIS 2001] [166, US EPA 2010] [171, WEF 2009] [222, CWW TWG 2013] [227, CWW TWG 2009] [231, US EPA 2008] [242, VEOLIA 2010] [243, SIEMENS 2007] [251, Ullmann's 2000]

3.3.2.3.5.5   Nitrogen removal by nitrification/denitrification

Description
Nitrogen, or more precisely ammonium, is removed by a special biological treatment that consists of two steps:

- the aerobic nitrification, where special microorganisms oxidise ammonium (NH_4^+) to the intermediate nitrite (NO_2^-) that is further converted to nitrate (NO_3^-);
- the anoxic denitrification, where microorganisms convert nitrate into 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 given in Table 3.122.

Table 3.122: Substantial inhibitors to nitrification

Compound	Inhibition concentration (mg/l) dissolved	Reduction in rate (%)
Allyl alcohol	20	50
Allyl isothiocyanate	1	50
Allylthiourea	1	50
p-Aminopropiophenone	43	50
Ammonia-N	200	50
Benzene	500	None
Benzidine dihydrochloride	20–100	50
Benzocaine	> 100	50
p-Benzoquinone	10	50
Benzylamine	> 100	50
Benzyl thiouronium chloride	20–100	50
2,2-Bipyridine	16/20	50
Carbon disulphide	20–100	50
Cetylpyridinium chloride	20–100	50

Compound	Inhibition concentration (mg/l) dissolved	Reduction in rate (%)
Cetyltrimethylammonium	20	50
Chlorobenzene	100	None
Chromium (VI)	0.25	Starting point
Copper	0.005–0.5	Starting point
Cresols	20	50
Cyanide	0.34	Starting point
Diallyl ether	20–100	50
1,1-Dichloroethane	125	Starting point
1,1-Dichloroethene	75	None
trans-1,2-Dichloroethene	75	None
Dichlorophen	20–100	50
Dicyandiamide	> 100	50
Diguanide	20–100	50
Dimethyl phthalate	100	None
Dimethylglyoxime	> 100	50
Dithiooxamide	1	50
Dodecylamine	< 1	50
Ethylenediamine	17	50
Ethylenediaminetetraacetate (EDTA)	350	50
Guanidine carbonate	20	50
Hexamethylenediamine	85	50
Hydrazine	20–100	50
8-Hydroxyquinoline	20–100	50
Lead	0.5	Starting point
Mercaptobenzothiazole	1	50
Mercury	1	Starting point
N-Methylalanine	1	50
N-Methylalanine hydrochloride	550	NI
Methylamine	< 1	50
Methylene blue	100	50
Methyl isocyanate	1	50
Methyl thiouronium sulphate	10	50
Monoethanolamine	> 100	50
Naphthalene	50	None
1-Naphthylamine	15	50
(Naphthyl)ethylenediamine dihydrochloride	23	50
Ninhydrin	> 100	50
p-Nitroaniline	31	50
p-Nitrobenzaldehyde	87	50
Phenol	3	30
p-Phenylazoaniline	72	50
Potassium thiocyanate	300	50
Pyridine	20	50
Quinoline	10	50
Skatole	10	50
Sodium azide	20–100	50
Sodium cyclopentamethylene thiocarbamate	20	50
Sodium dimethyldithiocarbamate	20	50
Sodium methyldithiocarbamate	1	50
Streptomycin	400	50
Strychnine hydrochloride	> 100	50
Tannic acid	> 100	50
Tetrachloromethane	50	None
Tetramethylthiuram disulphide	20–100	50
Tetramethylthiuram thiocarbamate	20	50
Thioacetamide	1	50
Thiosemicarbazide	1	50
Thiourea	1	50

Compound	Inhibition concentration (mg/l) dissolved	Reduction in rate (%)
Toluene	350	Starting point
2,4,6-Tribromophenol	> 100	50
Trichloromethane	18	75
Triethylamine	127	50
Trimethylamine hydrochloride	> 100	50
Zinc	0.08–0.5	NI
NB: NI = no information provided.		
Source: [3, Environment Agency (England and Wales) 1997].		

When nitrification/denitrification is carried out, it can typically be incorporated into a biological WWTP. A vital factor for denitrification is the ratio of oxygenated nitrogen (nitrate/nitrite) and BOD (as a reducing agent). A BOD/TKN ratio of four or greater is sufficient for nitrification/denitrification to occur [230, US EPA 2008]. There are two major layout options:

- the 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 3.44);
- denitrification as the 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 being recycled to the denitrification zone (see Figure 3.45).

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 WWTPs by constructional alterations, such as:

- installation of separation walls;
- installation of return pipes for waste water which contains nitrate;
- reuse of existent tank volume;
- usage of existing clarifier;
- adjustment or adaptation of process control.
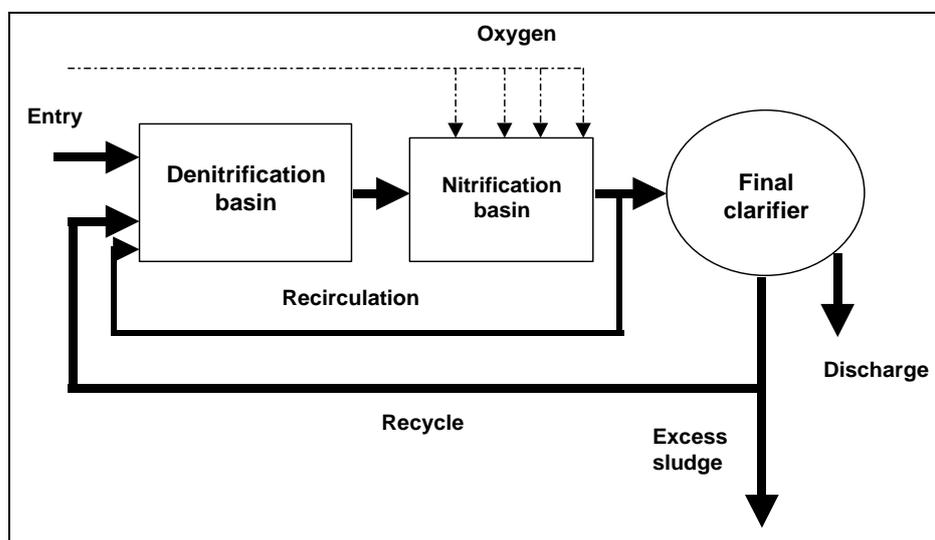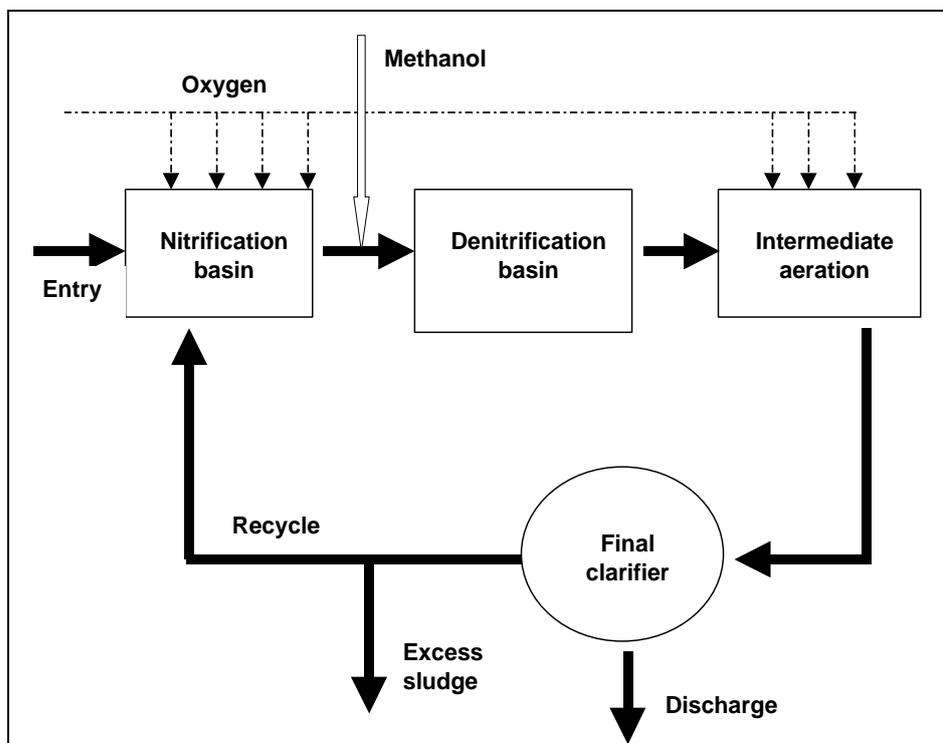
Figure 3.45: Example layout for nitrification/denitrification with denitrification as the first stage

Achieved environmental benefits
Achieved environmental benefits associated with nitrification/denitrification are given in Table 3.123.

Table 3.123: Abatement efficiencies and emission levels associated with nitrification/denitrification

Parameter	Abatement efficiency (%)	Emission level (mg/l)
Total N	60–> 95 % ([1, 2])	5–10 ([1])

([1]) [63, VITO 2010].
([2]) [1, Metcalf and Eddy 1991].

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 (see Section 3.5.5.4).

Nitrification/denitrification implies the consumption of energy. In some cases, an external carbon source needs to be added.

Common noise sources such as pumps, jets and mixers should be considered and appropriate measures taken, e.g. enclosure of equipment.

Operational data

Monitoring

Monitoring of a biological waste water treatment plant is illustrated in Section 3.2.2.1.

Applicability

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 the surface water (e.g. rivers), because the conversion of ammonium to ammonia, dependent on pH, results in fish toxicity.

Application limits and restrictions are given in Table 3.124.

Table 3.124: Application limits and restrictions associated with nitrification/denitrification

Issue	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 3.122)
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]) [87, UBA DE 2000].	

Advantages and disadvantages are given in Table 3.125.

Table 3.125: Advantages and disadvantages associated with nitrification/denitrification

Advantages	Disadvantages
• Effective elimination of nitrogen compounds • Process can be integrated into the existing biological treatment • Existing plants can easily be retrofitted	• Operation sensitive to varying conditions, pH, temperature, inhibitors (see Table 3.122), waste water contents • Gaseous releases to air

Economics

No information provided.

Driving force for implementation

Member States' legislation to reduce eutrophication of fresh waters.

Example plants
Sectors where the removal of nitrogen by nitrification/denitrification is used include chemical plants, municipal waste water treatment plants, the food industry, and composting installations.

Reference literature
[1, Metcalf and Eddy 1991] [3, Environment Agency (England and Wales) 1997] [63, VITO 2010] [87, UBA DE 2000] [227, CWW TWG 2009] [230, US EPA 2008]

3.3.2.3.5.6   Enhanced biological phosphorus removal

Description
Enhanced biological phosphorus removal is accomplished by sequencing and producing the appropriate environmental conditions in the reactors. During secondary biological treatment, 10 % to 30 % of the influent phosphorus is removed. Under certain operating conditions, more phosphorus than is needed may be taken up by the microorganisms, which is known as the 'luxury uptake'. Under anaerobic conditions, the microorganisms break the high-energy bonds in internally accumulated polyphosphate, resulting in the release of phosphate and the consumption of organic matter in the form of volatile fatty acids (VFAs) or other easily biodegradable organic compounds. When the microorganisms are then put under aerobic conditions, they take up phosphate, forming internal polyphosphate molecules. This luxury uptake results in more phosphate being included in the cells than was released in the anaerobic zone, so the total phosphate concentration in the solution is reduced. When the microorganisms are wasted, the contained phosphate is also removed. A sufficient supply of VFAs is the key to removing phosphorus biologically.

Biological phosphorus removal can be accomplished in conjunction with treatment plants that nitrify and/or denitrify, with and without primary sedimentation. Where both nitrogen and phosphorus are to be removed, combination processes are used most commonly.

Achieved environmental benefits
Reduction in the effluent phosphorus content.

Cross-media effects
None.

Operational data
No information provided.

Applicability
A key factor in determining the cost-effectiveness of biological phosphorus removal is the relative amount of organic material that can be used by the microorganisms, namely phosphate-accumulating organisms. A COD/TP ratio of 45 and a BOD/TP ratio of 20 are the minimum values needed to meet a 1 mg/l TP limit. If VFAs have been detected, a minimum VFA/TP ratio of at least 4 is recommended to obtain good biological phosphorus remova

Economics
No information provided.

Driving force for implementation
To reduce the potential for eutrophication of fresh waters.

Example plants
Enhanced biological phosphorus removal is used by a number of urban waste water treatment plants in the EU. No example plant from the chemical sector was reported.

Reference literature
[1, Metcalf and Eddy 1991] [230, US EPA 2008]

3.3.2.3.5.7 Phosphorus removal by chemical precipitation

Description
The chemical precipitation of phosphorus is accomplished by the addition of the salts of multivalent metal ions that form precipitates of sparingly soluble phosphates. The multivalent metal ions used most commonly are calcium (Ca^{2+}), aluminium (Al^{3+}) and iron (Fe^{3+}). General aspects of chemical precipitation are described in Section 3.3.2.3.4.2.

Chemical addition occurs in primary clarifiers (when present) or in the secondary process, in the aeration basin or upstream of the secondary clarifiers, or in tertiary clarifiers or other treatment processes. Feeding chemicals to the primary clarifiers usually requires less chemical use than feeding to the secondary or tertiary process. Feeding chemicals at both the primary and secondary clarifiers results in less chemical use than feeding to the secondary process alone, allowing some phosphorus to be removed in the primary clarifiers and polishing to occur in the secondary process. The resulting chemical precipitate will settle to the tank bottom where it can be removed as a sludge.

Achieved environmental benefits
Reduction in the effluent phosphorus content.

Cross-media effects
The resulting chemical sludge that needs to be disposed of and treated, the cost of chemicals used and the accumulation of ions (increased salt content) may seriously restrict the reuse of effluent.

Operational data
No information provided.

Applicability
No information provided.

Economics
No information provided.

Driving force for implementation
To reduce the potential for eutrophication of fresh waters.

Example plants
WWTPs #06, #34 and #36.

Reference literature
[1, Metcalf and Eddy 1991] [230, US EPA 2008]

3.3.2.3.6 Rainwater and firefighting water collection and treatment

3.3.2.3.6.1 Overview

An essential point for industrial activities is the prevention of uncontrolled effluents from the site, such as contaminated rainwater or firefighting water. For this purpose, the drainage system of an industrial site can be divided into a production surface part, including:

- non-roofed production plant surfaces,
- areas of storage tanks,
- roofed production plant surfaces exposed to contamination/pollution,

and a normal traffic surface part, such as:

- roads inside the site,
- the administration area,
- uncontaminated roof surfaces,
- parking areas.

Rainwater from production areas and firefighting water is collected either in sumps on the spot or in other central facilities (e.g. emergency storage tanks or lagoons) to allow inspection and then a decision is to be made on whether to discharge it directly to the receiving water or to a waste water treatment facility. Parameters to monitor and pollution prevention techniques to be applied based on the monitoring results will depend in particular on the activities carried out at the site and their significance to any receiving water as well as on the rainfall intensity and duration, which have major regional variations. Typical parameters that may be monitored rapidly during periods of rainfall are, for example, pH, turbidity, TOC, colour, and floating material. The frequency of monitoring (e.g. continuous or regular) depends on a combination of several factors such as the frequency of rainfall, the size of the installation (SMEs are generally less likely to use continuous monitoring and have more difficulties in storing rainwater), as well as the activities carried out at the installation and their significance to any receiving waters. Continuous monitoring may not be economically viable at small installations with small volumes of rainwater compared to the total volume of waste water to be treated. These installations may choose to systematically send rainwater to treatment irrespective of whether it is contaminated or not [107, COM 2007].

Rainwater collection, monitoring and discharge is generally a matter of routine at industrial sites, characterised both by the relatively low potential chemical pollution of the water and the low EHS risks associated. Dealing with firefighting water, especially from chemical installations, presents potential EHS risks of another nature that may necessitate specific measures. Specific legislation exists addressing this issue (e.g. the Seveso Directive [145, EU 2012]).

Techniques primarily designed for catching spillages and wash waters from cleaning, are also used to catch contaminated rainwater or firefighting water from production or other areas such as:

- concrete or asphalt bases with sealed liners or impermeable paints;
- bunded areas or basements for production areas;
- retention ponds.

Information on techniques used to prevent the contamination of rainwater from storage areas can be found in the Emissions from Storage BREF [113, COM 2006].

Depending on the pollutant load, contaminated rainwater and firefighting water can be treated using physico-chemical and/or biological treatment.

For contaminated rainwater, an option is to collect the first flush of stormwater in a storage tank and direct it to the treatment plant slowly; the overflow is discharged to the receiving water. In the case of sensitive rivers, the flow rate of the stormwater discharge/overflow should be limited to prevent erosion of the riverbed.

Care needs to be taken to prevent the collection of firefighting water from causing fire to spread.

The drainage system of normal traffic areas is, where appropriate, connected to extra discharge facilities that are, for example, installed to:

- protect the receiving water against the hydraulic load from the run-off of large paved areas during heavy rainfall;
- remove flushed contaminant fallout accumulated during dry periods;
- prevent the unintentional discharge of accidental spillages 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.

3.3.2.3.6.2 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 a strain on the receiving water downstream. 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 spillages, retention ponds are equipped with oil separation/interception facilities.

Achieved environmental benefits
Retention ponds enable the removal of pollutants from rainwater run-off as well as preventing a strain on the receiving water downstream.

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
Normally, sedimented sludge has to be disposed of. Easily biodegradable substances collected within the retention pond can cause odour emissions.

Operational data
Monitoring
Proper maintenance will ensure the continued accurate functioning of the retention pond. This includes [17, US Navy 1998]:

- clearing rubbish and debris;
- conducting routine inspections of the embankment and spillway to check the structural integrity and to look for signs of erosion or animal habitation;
- conducting periodic repairs on the embankment, emergency spillway, and the 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.

Applicability
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, however, in existing installations space requirements can be a restriction.

Advantages and disadvantages are given in Table 3.126.

Table 3.126: Advantages and disadvantages associated with retention ponds

Advantages	Disadvantages
• For discharges into weak recipients, retention ponds decrease the potential for downstream flooding and riverbank erosion	• First flush systems provide no spillage containment, i.e. space is required for sufficient volumes

Economics
The investment costs associated with retention ponds are reported to be significant depending on the required basin capacity and the type of facility [226, US EPA 1999]. Both the investment costs and the operating and maintenance costs are highly dependent on the intensity, duration and frequency of the rainfall which directly affects the required volume of the retention pond.

Driving force for implementation
The main driving force for implementation of the technique is to preserve surface water quality.

Example plants
No information provided.

Reference literature
[17, US Navy 1998] [226, US EPA 1999]

3.3.2.3.6.3   Sand filters

Description
Sand filters are applied 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.

Achieved environmental benefits
Achieved environmental benefits associated with sand filters are given in Table 3.127.

Table 3.127: Abatement efficiencies and emission levels associated with sand filters

Parameter	Abatement efficiency (%)	Emission level (mg/l)
TSS	80–83 ([1])	< 10 ([2])
([1]) [17, US Navy 1998].		
([2]) [235, CASQA 2003].		

Effluent concentration (i.e. emission level) for suspended solids is relatively constant and independent of influent concentration. Consequently, the performance is more accurately characterised by the effluent concentration than by the abatement efficiency.

Cross-media effects
Backwashed sludge has to be disposed of as waste.

Operational data
Monitoring
The 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.

Applicability
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.

The limit of application is typically 50–100 ppm of solids because of the quantity of backwash water necessary [227, CWW TWG 2009].

Advantages and disadvantages are given in Table 3.128.

Table 3.128: Advantages and disadvantages associated with sand filters

Advantages	Disadvantages
- High removal efficiencies achievable - Low space requirements	- Substances dissolved in water are not removed, unless by adsorption

Economics
The investment costs are dependent on the chosen sand filter system and vary widely. Annual costs for maintaining sand filter systems average about 5 % of the initial construction cost. Filter media are replaced as needed [221, US EPA 1999].

Economics associated with sand filters are given in Table 3.129.

Table 3.129: Economics associated with sand filters

Type of costs	Costs	Comments
Investment costs	USD 18 500–240 000 (EUR 16 200–210 000) ([1, 2])	Depending on the size of the drainage area
	EUR 50 000 ([3])	
Maintenance costs: Equipment and materials	USD 1013 (EUR 886) ([1])	–
Labour	43 h/yr ([1])	
([1]) Cost data for 1997 [235, CASQA 2003]. Average currency conversion rate for 1997: EUR/USD = 1.143. ([2]) USD 18 500 (EUR 16 200) for a 0.4 ha drainage area; USD 240 000 (EUR 210 000) for a 1.1 ha drainage area. ([3]) Continuous sand filtration (5 m^2 or about 50m^3/h) [63, VITO 2010].		

Driving force for implementation
The main driving force for implementation of the technique is to preserve surface water quality.

Example plants
Sand filters are successfully used in drinking water production, ground water treatment, municipal waste water treatment, surface treatment of metals, slaughterhouses, and the food and beverage industry.

Reference literature
[17, US Navy 1998] [63, VITO 2010] [221, US EPA 1999] [227, CWW TWG 2009] [235, CASQA 2003]

3.3.3 Combination of waste water treatment techniques

3.3.3.1 Activated sludge process

Description
A WWTP using the activated sludge process is normally equipped with:

- buffer or equalisation volumes (see Section 3.3.2.1), if not already provided by other upstream facilities;
- a mixing station, where neutralisation and flocculation chemicals (see Sections 3.3.2.1 and 3.3.2.3.3.3) are added and mixed (usually lime milk and/or mineral acids and ferrous sulphate), enclosed or covered if necessary to prevent releases of odorous substances, the captured exhaust air ducted to an abatement system;
- a primary clarifier, where the floc is removed (see Section 3.3.2.3.3.4), enclosed or covered if necessary to prevent fugitive releases of odorous substances, the captured exhaust air ducted to an abatement system;
- an activated sludge part (see Section 3.3.2.3.5.4), for example:
  - an aeration basin with a nutrient feed at the entry, enclosed or covered if necessary with exhaust air ducts to an abatement system,
  - or a closed reaction tank (e.g. tower biology) with a gas duct, connected to a gas abatement system,
  - a nitrification/denitrification stage (optional) and phosphate elimination;
- an optional intermediate clarifier, when a second aerobic biological stage is operated, with sludge recycling;
- an optional secondary activated sludge part, for low-load biology;
- a final clarifier with sludge recycling and transfer to sludge treatment (see Section 3.4.2); alternative sand filter (see Sections 3.3.2.3.3.6 and 3.3.2.3.6.3), MF or UF equipment (see Section 3.3.2.3.3.7);

- optionally further special treatment facilities to eliminate the rest of refractory TOC/COD, e.g. a biofilter (see Section 3.3.2.3.5.4);
- optionally further treatment facilities after the final clarifier, e.g. for air flotation (see Section 3.3.2.3.3.5);
- sludge treatment facilities, such as:
  ◦ digesters (see Section 3.4.2.3),
  ◦ sludge thickeners (see Section 3.4.2.2),
  ◦ sludge dewaterers (see Section 3.4.2.2),
  ◦ sludge incinerators (outside the scope of this document);
- exhaust air abatement facilities, such as:
  ◦ adsorbers (see Section 3.5.1.2.3),
  ◦ thermal or catalytic oxidisers (see Section 3.5.1.3.5 and Section 3.5.1.3.6),
  ◦ flares (see Section 3.5.1.6),
  ◦ biofilters or bioscrubbers (see Section 3.5.1.3.1 and Section 3.5.1.3.2).

An example of a WWTP using the activated sludge process is illustrated in Figure 3.46.

Source: [21, Kunz 1990]
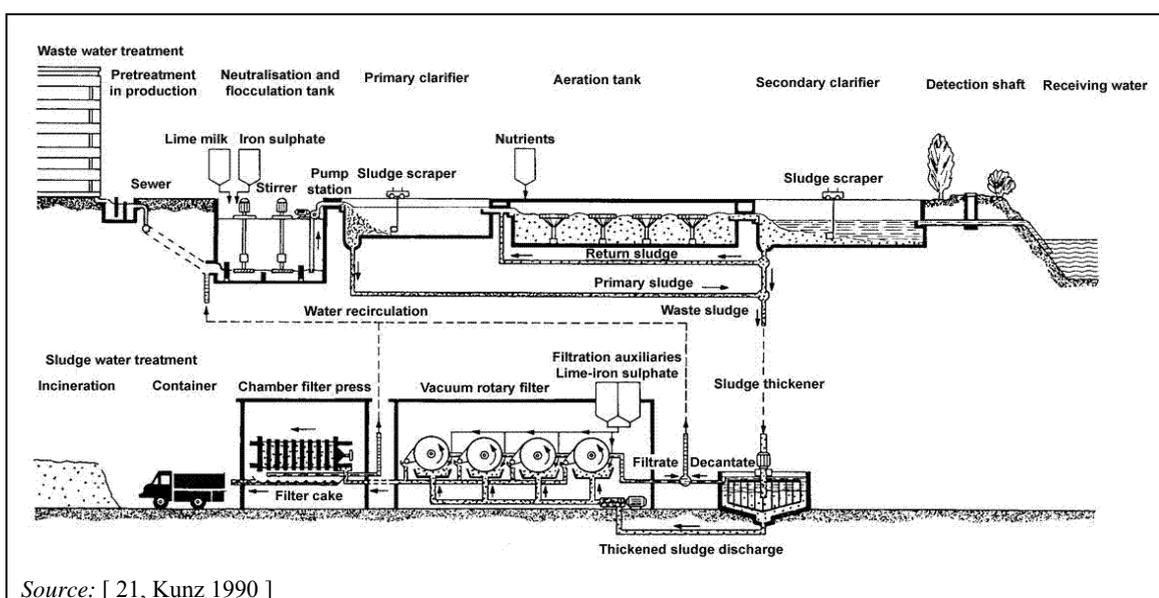
Figure 3.46: Example of a WWTP using the activated sludge process

Achieved environmental benefits
The main parameter to check the performance of biological treatment is BOD, while the degradation of TOC/COD depends on the degree of upstream pretreatment and the content of poorly degradable contaminants. Since refractory TOC/COD (or contaminant concentrations that act as refractory TOC/COD) is not suitable for biological treatment, and should therefore be left out as much as possible of a biological WWTP, it makes sense to list achievable TOC/COD levels.

Cross-media effects
As already described in Section 3.3.2.3.5.4, the main impacts of aerobic biological treatment are the energy consumption for aeration combined with mixing in the aeration basin, the arisings 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 emissions to air is enclosing or covering the sensitive areas such as the mixing station, the primary clarifier and the 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 associated with conventional activated sludge systems are given in Table 3.130.

Table 3.130: Consumables associated with activated sludge systems

Consumable	Amount
Air or oxygen	180–755 m^3 O$_2$/t influent COD (^{1}) 1.21–3.06 t O$_2$/t influent COD (^{1})
Neutralisation chemicals	150–17 900 t H$_2$SO$_4$ (75 %)/yr 10–1 500 t NaOH/yr
Flocculants	300–550 kg/t COD ($^{2, 3}$) 0.5–1.9 kg/t COD ($^{4, 5}$)
Nutrients	23–42 kg/t COD ($^{3, 6}$) 3–5 kg/t COD ($^{5, 6}$)
Energy (kWh/m^3)	9.5 ($^{3, 7}$) 0.7–4.0 (^{5}) 0.1 kWh per p.e. (^{8})
Energy (kWh/kg COD abated)	0.7–33.4 (^{1})

(^{1}) Information gathered from 21 questionnaires. In 12 of them, energy consumption values of < 1.5 kWh/kg COD abated were reported. In the following 6 questionnaires, values between 1.7 and 6.75 kWh/kg COD abated were reported, while values of 11.7 kWh/kg COD abated (WWTP #61, three-stage biological treatment), 18.4 kWh/kg COD abated (WWTP #69, includes MBR treatment) and 33.4 kWh/kg COD abated (WWTP #041, biological treatment with nitrification and partial denitrification) were reported in another 3 questionnaires [222, CWW TWG 2013]. At chemical sites, due to the energy flow throughout the site, the energy consumption figures tend to be highly site-specific.
(^{2}) Flocculant: ferrous sulphate.
(^{3}) [36, NOREC 2000].
(^{4}) Only waste water treatment part.
(^{5}) [41, Bayer 2000].
(^{6}) *o*-Phosphoric acid.
(^{7}) Including sludge incineration.
(^{8}) [63, VITO 2010].

The amount of sludge arising during the activated sludge process is not easy to quantify in relation to the contaminant load. It encompasses a large quantity of between 34 and 2 000 kg dry matter per tonne of COD eliminated, averaging in the range of 250–720 kg dry matter per tonne of COD eliminated [41, Bayer 2000].

Operational data
Monitoring
Monitoring of influent and effluent waste waters from a WWTP is detailed in Section 3.2.2.1.

Performance data gathered from the questionnaires have been analysed and the results of emission levels and abatement efficiencies for major parameters are presented in Chapter 2. The complete mix activated sludge process is the most frequently used biological treatment system [222, CWW TWG 2013]**.**

Example data from well-performing waste water treatment plants using an activated sludge process are shown in Table 3.131. For more details on the plant configurations see Section 7.2, Annex II.

Table 3.131: Example data from well-performing waste water treatment plants using an activated sludge process

Plant code	Location	BREFs	Year	Treated waste water volume in 10^3 m³/yr	Concentrations in mg/l (mostly yearly average)												
					Influent						Effluent						
					BOD$_5$	COD	TOC	TN	N$_{inorg}$	TP	BOD$_5$	COD	TOC	TN	N$_{inorg}$	TP	TSS
#01	DE	OFC	2007	1 400	2 100	3 300	780	NI	85	6.1	1.9	82	25	NI	9	0.29	6
#02	DE	CAK, LVIC-AAF, LVIC-S, LVOC, OFC, POL, SIC	2007	120 000	640	1 200	419	NI	95	8.0	< 4	63	22	NI	12	0.99	11
#03	DE	CAK, LVOC, POL	2011	10 000	200	570	NI	NI	24	21	2	34	13	7	6.6	0.91	6
#07	DE	OFC	2007	3 000	1 000	NI	580	NI	75	4.8	5	NI	32	NI	7	0.6	11
#12	DE	OFC	2011	2 200 ([1])	590 ([1])	920	NI	NI	37	8.9	4 ([1])	26	NI	NI	3	0.36	NI
#13	DE	OFC	2011	2 700	NI	760	NI	NI	NI	NI	NI	42	NI	NI	2.7	0.21	NI
#19	NL	OFC	2007	630	760	1 400	NI	NI	NI	NI	15	160	NI	9	NI	0.8	19
#40	FR	OFC, POL	2011	580	NI	1 000	NI	NI	NI	NI	8	61	NI	38 ([2])	34	0.8	13
#45	IT	LVIC-AAF, LVIC-S, LVOC, OFC, POL	2007	11 000	NI	630	NI	NI	NI	NI	6.3	79	NI	8.3	3.5	0.5	22
#49	BE	CAK, LVIC-AAF, LVOC, POL	2011	12 000	710	1 200	430	190	NI	3.7	10	110	37	18	NI	3.0	21
#52	BE	POL	2007	120	2 500	3 100	NI	170	NI	3	7.5	67	NI	28	NI	1.8	NI
#60	FR	OFC, POL	2011	270 ([1])	NI	3 000	NI	NI	NI	NI	5	120	NI	14 ([3])	10 ([3])	0.55 ([3])	20
#62	CZ	LVOC, POL	2011	130 ([1])	NI	NI	NI	NI	NI	NI	4.5	27	NI	NI	1.3	NI	8
#63	CZ	LVIC-AAF, LVOC, POL	2011	6 300	770	910	NI	85	NI	NI	3.3	21	NI	3.6	2.6	0.69	7.7
#64	FR	LVOC, OFC, POL	2007	4 700	350	900	NI	NI	NI	NI	11	110	NI	7	NI	NI	18
#75	DK	OFC	2011	160	3 900	NI	1 900	84	NI	NI	7	NI ([1])	54	5	NI	0.8	10
#91	IT	LVOC, POL	2011	9 200	480	600	NI	1	0.7	3	20	40	NI	0.5	0.5	1	20
#96	PL	LVIC-AAF, LVOC	2011	2 400	680	1 500	NI	370	340	NI	5.4	54	NI	38	35	0.18	14

([1]) In 2007.
([2]) TN elimination in loads: 70 % in 2011.
([3]) In 2008.

NB: BOD$_5$ = biochemical oxygen demand after five days; COD = chemical oxygen demand; NI = no information provided; N$_{inorg}$ = total inorganic nitrogen; TN = total nitrogen; TOC = total organic carbon; TP = total phosphorus; TSS = total suspended solids.

Source: [222, CWW TWG 2013]

Applicability
The activated sludge process is applied to complex waste water originating from the production and handling of organic chemicals, provided the content is biodegradable. It is a common end-of-pipe technique in the chemical industry, which is able to remove the following contaminants: suspended solids, biodegradable compounds, and nutrients (i.e. nitrogen, phosphorus).

Waste water with a considerable amount of contaminants not belonging to these groups needs either pretreatment before being discharged to the activated sludge process or special treatment (see Section 3.3.2.3.4) and bypassing. Waste water which contains an exceedingly high biodegradable load is also normally pretreated (see Sections 3.3.2.3.5.2 to 3.3.2.3.5.5).

For application limits and restrictions, see Sections 3.3.2.3.5.4 and 3.3.2.3.5.5:

Advantages and disadvantages are given in Table 3.132.

Table 3.132: Advantages and disadvantages associated with conventional activated sludge systems

Advantages	Disadvantages
• Large amounts of waste water treated • Synergistic effects can increase efficiency • Energy efficiency is high compared to processes such as GAC adsorption, incineration and wet oxidation. Energy is mainly supplied by sustainable methods (metabolism of microorganisms with air and water) • Degradation normally into less harmful compounds (there are some exceptions when degradation products react to new compounds and occasionally 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 amounts of excess sludge should be disposed of • The aeration process causes stripping effects for volatile compounds resulting in fugitive odorous and/or aerosol releases

Economics
Economics associated with conventional activated sludge systems are given in Table 3.133 [222, CWW TWG 2013].

Table 3.133: Economics associated with conventional activated sludge systems

Type of costs	Costs
Investment costs	EUR 2.5–33 million
Operating costs (i.e. operation, maintenance, consumables including energy, laboratory) without sludge disposal costs	EUR 0.6–5.7/m^3 of waste water treated ([1])
Disposal of sludge	EUR 0.2–1.4/kg dry matter
([1]) At chemical sites, due to the energy flow throughout the site, the energy consumption figures tend to be highly site-specific.	

Investment and operating costs depend to a great extent on the complexity of preparatory and subsequent separation operations surrounding the biological treatment.

Driving force for implementation
The technique is used to reduce the organic load discharged to the receiving water and thus to comply with legislation on water quality standards.

Example plants
Conventional activated sludge systems are extensively used as the central waste water treatment in many industrial sectors and also in municipal waste water treatments. Example installations are listed in Section 2.2 and Section 7.2, Annex II.

Reference literature
[21, Kunz 1990] [36, NOREC 2000] [41, Bayer 2000] [63, VITO 2010] [222, CWW TWG 2013]

3.3.3.2 Membrane bioreactor

Description
The membrane bioreactor (MBR) process is an alternative to conventional activated sludge processes for biological waste water treatment (see Section 3.3.3.1) and an option of choice for many domestic and industrial applications. MBR consists of the combination of a membrane process (e.g. microfiltration or ultrafiltration) with a suspended growth bioreactor. In an MBR system for biological waste water treatment, the secondary clarifier and the tertiary filtration step of a traditional aerated sludge system is replaced by membrane filtration (the separation of sludge and suspended solids). Typical arrangements consist of vacuum-driven membrane units submerged in the aerated portion of the bioreactor or pressure-driven membrane systems located outside the bioreactor (see also Section 3.3.2.3.5.4). Membranes are typically configured hollow tube fibres or flat panels and have pore sizes ranging from 0.1 to 0.4 microns.

Achieved environmental benefits
The achieved environmental benefits of the use of a membrane bioreactor include:

- reduction of the load of suspended solids, COD, BOD, TOC, TP by 95–99 %;
- reduction of the microbiological health risk to levels that comply with Directive 2006/7/EC concerning the management of bathing water quality [70, EC 2006];
- reduction of the volume of sludge compared to conventional aerated sludge treatment;
- reduction of the plant footprint compared to conventional aerated sludge treatment, especially if tertiary filtration and a UV disinfection unit would be necessary to achieve comparable output quality.

Data on the environmental performance of MBRs compared to other biological treatment systems can be found in Section 3.3.2.3.5.4.

Cross-media effects
Cross-media effects include energy consumption (mainly for pumping and aeration), chemical consumption (for membrane cleaning) as well as membrane replacement.

Operational data
As with other membrane separation processes, membrane fouling is the most serious problem affecting the performance of MBR systems. Fouling leads to a significant increase in hydraulic resistance, manifested as permeate flux decline or transmembrane pressure (TMP) increase when the process is operated under constant TMP or constant flux conditions, respectively.

Frequent membrane cleaning and replacement is therefore required, increasing the operating costs significantly. Membrane fouling results from an interaction between the membrane material and the components of the activated sludge liquor, which include biological flocs formed by a large range of living microorganisms along with soluble and colloidal compounds. Although different membrane manufacturers use different techniques to control fouling, the primary method to address fouling is aeration along with periodic chemical cleaning. Membrane aeration to control fouling was reported to account for 35 % to 40 % of the total power consumption of an MBR [166, US EPA 2010].

MBR is key to the central biological waste water treatment in the Roche Diagnostics GmbH chemical plant in Penzberg, Germany. The plant produces biopharmaceutical ingredients using biological processes [222, CWW TWG 2013]. The central biological waste water treatment consists of the following steps:

Step 1: high-performance activated sludge treatment of highly polluted waste water from production plants after balancing the concentration (aeration system using refined oxygen).

Step 2: activated sludge treatment of waste water from production plants (after neutralisation) plus effluents from Step 1, plus sanitary waste water after mechanical treatment (screening). Step 2 consists of six aeration tanks operated as a biological cascade; the last tank is designed as a membrane bioreactor.

The plant has a treatment capacity of 3 800 m^3/d and can treat 4 800 kg BOD_5/d. The average waste water flow treated in 2007 was 1 366 m^3/d. Performance data of the plant are given in Table 3.134.

Table 3.134: Example of environmental performance of a central biological WWTP including a membrane bioreactor

Parameter monitored	Output from the central biological treatment		Elimination rate (%)
	Concentration (mg/l as a yearly average)	Load (kg/d as a yearly average)	
TOC	12.1	16.7	95.2
BOD_5	1	1.4	99.7
COD	28.3	39	95.2
Total inorganic nitrogen (N_{inorg})	6.9	10	88.6
Nitrate (NO_3-N)	6.9	NI	NI
TP	1.2	1.6	95.2
Chloride	745	1 016	NI
Sulphate	117	160	NI
Toxicity (dilution factor):			
Fish or fish egg	1		NI
Daphnia	1		NI
Algae	1		NI
Luminescent bacteria	1		NI
NB: NI = no information provided.			
Source: [222, CWW TWG 2013]			

Management of emergency situations:

- buffer tanks (in total: 450 m^3).

Waste gas treatment:

- closed design of all compartments of both steps with the exception of three tanks belonging to the activated sludge plant of Step 2; closed design of MBR;
- biofilter treatment of highly odorous waste gases.

A chemical site in Germany at which the production of pharmaceuticals and metal alkyls is carried out employs MBR technology for biological treatment (WWTP #36). The WWTP started operation in 2004, treating 1.2 million m^3 of waste water annually. The WWTP achieves more than 99 % BOD removal and approximately 90 % COD removal [222, CWW TWG 2013].

In France, two Sanofi-Chimie facilities located in Aramon and Sisteron have been using MBR systems (retrofits of conventional activated sludge systems) since the year 2000. The plant in Aramon produces a large range of pharmaceutical products and has two MBRs in parallel, each having a volume of 3 600 m^3. The aeration tank is divided into three parts: a high-rate activated sludge zone where COD removal and nitrification are carried out, an anoxic zone where denitrification is carried out and a low-rate activated sludge zone where poorly biodegradable COD is removed [218, INERIS 2010].

The plant has a treatment capacity of 1 200 m^3/d and can treat up to 15 000 kg COD/d. The average waste water flow treated in 2009 was 1 085 m^3/d. The influent COD load is in the range of 3–30 g/l (8.7 g/l in average), with a fairly important variability (mainly due to the variability of the production of the facility). Performance data of the plant are given in Table 3.135 and the variability in the influent and effluent concentrations of certain pollutants are given in Table 3.136.

Table 3.135: Example of environmental performance of a membrane bioreactor treating waste waters from a plant producing pharmaceutical products

Parameter monitored	Output from the central biological treatment – yearly average (2009)		Elimination rate (%)
	Concentration (mg/l)	Load (kg/d)	
TSS	2.9	3	97.9
BOD$_5$	2	2.1	99.9
COD	285	313	96.3
TOC	57 (TOC = COD/5)	63 (TOC = COD/5)	NI
AOX	0.27	0.3	NI
TN (as N)	12	13	NI
Ammonia (NH$_4$-N)	3.2	3.5	NI
TP ([1])	18.5	19.5	NI
Chloride	3 500	3 845	NI
([1]) A project planned for the year 2011 was intended to improve the performance of P removal. NB: NI = no information provided. *Source:* [218, INERIS 2010]			

Table 3.136: Variability of influent and effluent concentrations of a membrane bioreactor treating waste waters from a plant producing pharmaceutical products

	Flow (m^3/d)	COD (mg/l)			BOD$_5$ (mg/l)			TSS (mg/l)		AOX
		Input WWTP	Input MBR	Output	Input WWTP	Input MBR	Output	Input WWTP	Output	Output
Yearly average	1 100	8 700	6 700	285	4 800	3 800	2	145	3	0.3
Min. monthly average ([1])	800	7 600	5 100	240	3 700	2 700	1.9	109	< LOQ	0.1
Max. monthly average ([1])	1 180	10 700	7 800	385	6 600	4 700	2.6	192	14	0.7
90th percentile (yearly ave.) ([2])	NI	NI	NI	275	NI	NI	NI	NI	NI	NI
([1]) Min./Max. monthly average means minimum/maximum of the 12 monthly averages of the year, determined without removing abnormal discharges. ([2]) The 90th percentile value is calculated as follows: on a monthly basis, the 10 % highest values are filtered out to calculate the monthly average. Then, the yearly average is calculated normally from these monthly averages. NB: NI = no information provided. *Source:* [218, INERIS 2010]										

Consumables are given in Table 3.137.

Table 3.137: Consumables associated with a membrane bioreactor treating waste waters from a plant producing pharmaceutical products

Consumable	Amount
Air or oxygen	6 350 m^3 equivalent O_2/t COD treated 6.3 t eq. O_2/t COD treated ([1]) (at bioreactor level)
Neutralisation chemicals	~ 1 200 t equivalent HCl (36 %)/yr (of which 90 % is recovered) ([2]) ~ 1 200 t equivalent NaOH (30 %)/yr (of which 70 % is recovered on site)
Flocculants	Approximately 10 kg/t COD
Nutrients	Negligible (N+P in summertime)
Energy (whole WWTP) ([3])	12.5 kWh/m^3 1.6 kWh/kg COD eliminated
Energy (MBR only) ([3])	3.8 kWh/m^3 (=30 % of the WWTP total consumption)

([1]) Air is injected at 80 $^{\circ}$C, 1 000 m^3 of O_2 = 1 t of O_2.
([2]) HCl is recovered from the nearby waste incineration process and used as acid for neutralisation.
([3]) Without including sludge incineration.
Source: [218, INERIS 2010]

Applicability

The membrane bioreactor technique is applicable after highly efficient mechanical pretreatment (maximum screen width of 1 mm) and for the removal of biodegradable compounds, suspended solids and microbial contaminants. It can be combined with nitrogen and phosphorus elimination. Membrane bioreactors can be applied when retrofitting existing plants or for new installations.

Advantages and disadvantages are given in Table 3.138.

Table 3.138: Advantages and disadvantages associated with membrane bioreactor

Advantages	Disadvantages
• Smaller space requirements • Reduced amount of sludge (compared to conventional activated sludge system) • For medium to highly loaded influents (3 to 30 g/l of COD), a major benefit of MBR treatment plants is the ability to keep a good efficiency with inlet COD variations, whereas keeping the same performance with a conventional activated sludge plant requires larger equalisation tanks than with MBRs [218, INERIS 2010] • Contrary to a conventional clarifier, the MBR system may act as a physical barrier in upset conditions [218, INERIS 2010] • Can operate at much higher solids concentrations (typically 8 000–12 000 mg/l) compared to the conventional activated sludge system (typically 3 000–6 000 mg/l) [227, CWW TWG 2009] • Once abrasion and pressure variations are under control, ceramic membranes have constant performance without aging loss [218, INERIS 2010]	• High running costs (energy) because of the high pressure drop and high air-flushing rate required for its operation • Membranes are sensitive to abrasion so, when retrofitting an existing WWTP with a MBR unit, it should be verified that abrasion will not occur (e.g. the quality of the concrete of the tanks should be checked) [218, INERIS 2010] • Silicones in the influent must be prohibited as they rapidly plug the membranes [218, INERIS 2010] • Pressure variations must be controlled as membranes are quite sensitive and can break [218, INERIS 2010]

Economics
The cost of an MBR plant for secondary processing is still higher than that of a conventional activated sludge plant, but as the numbers of MBR plants increase, and as membrane costs fall, the life cycle cost differential should soon disappear, and the process advantages should lead to rapid uptake of the MBR system by the waste water treatment industry [214, Sutherland 2009].

However, operation and investment costs may in concrete cases be lower than for conventional activated sludge systems designed for comparable output quality. Individual cost assessments have to be performed on a case-by-case basis.

In the case of the Roche example plant above, an existing traditional two-step aerated sludge system with a treatment capacity of 1 000 m^3/d was upgraded, resulting in a capacity of 3 800 m^3/d, by adding additional aerated tanks and designing the last tank as a MBR. Energy consumption has since declined by 1.8 kWh/m^3 and 2.3 kWh/kg of BOD_5 eliminated, when compared to the consumption before reconstruction (the energy consumption for the Roche example plant is 3.6 kWh/m^3 of waste water treated and 3.1 kWh/kg of BOD_5 eliminated).

In the Aramon example plant, the operating costs (excluding sludge disposal costs) are reported to be EUR 4–6/m^3 and EUR 600–800/t of COD removed. The cost of disposal of sludge is around EUR 100 per tonne of sludge.

Driving force of implementation
Reasons for implementing the technique include:

- reconstruction of an existing waste water treatment plant to enlarge the treatment capacity;
- improvement of output quality with respect to the organic load (reduction of waste water charge); voluntary action (i.e. no legal requirement);
- improvement of output quality with respect to microbial contaminants (discharge into surface water publicly used for bathing/leisure activities); voluntary action (i.e. no legal requirement);
- a cost assessment based on the results of pilot plant operation which identified MBR as the most cost-effective design;
- compliance with Directive 2006/7/EC concerning the management of bathing water quality [70, EC 2006].

Example plants
In addition to the abovementioned examples, MBRs are also in use in Varsseveld, the Netherlands.

There are now well over 1 000 MBRs in use worldwide, although a significant number of these are only of pilot scale [214, Sutherland 2009].

Reference literature
[70, EC 2006] [138, UNSW 2009] [166, US EPA 2010] [214, Sutherland 2009] [218, INERIS 2010] [222, CWW TWG 2013] [227, CWW TWG 2009]

3.3.3.3   Removal and reuse of nitrate from waste water

Description
At a large chemical site in Germany producing CuZn, Ni and CuCr catalysts, waste waters which contain high concentrations of nitrate are first pretreated and then undertake a combination of reverse osmosis (RO), evaporation and crystallisation processes in order to recycle valuable sodium nitrate. The pretreatment and subsequent operations are carried out in the so-called NITREA® treatment plant (see Figure 3.47).

Source: [137, LAWA 2008]
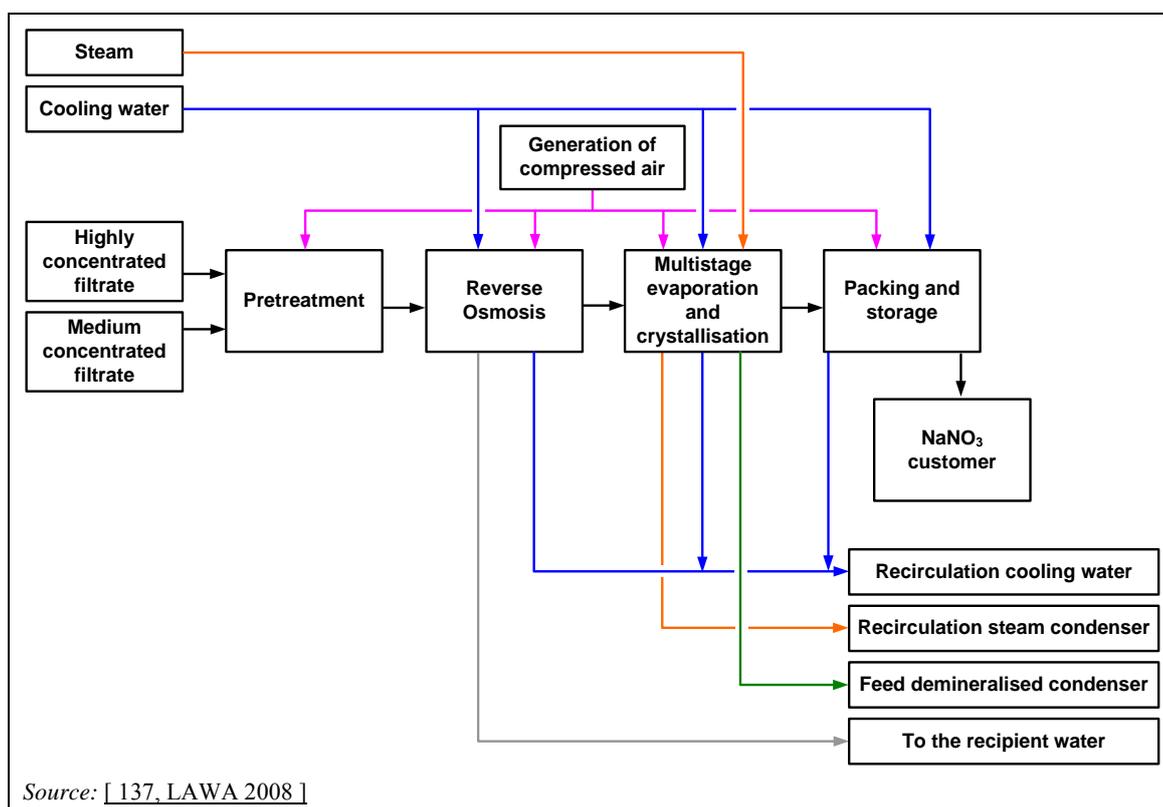
Figure 3.47: NITREA® treatment plant flow scheme

The chemical plant generates waste waters which contain only inorganic substances (i.e. heavy metal ions, fine crystalline solid substances, sodium ions, ammonium ions, nitrate carbonate and chloride).

The waste water volume entering the NITREA® treatment plant consists of:

- a highly concentrated filtrate (i.e. 82 m^3/d and 13 700 mg/l of nitrate);
- a medium concentrated filtrate (i.e. 150 m^3/d and 1 000 mg/l of nitrate).

To obtain a pure, marketable sodium nitrate, all impurities have to be removed before bringing the waste water into the RO. This pretreatment is carried out as follows:

- pH adjustment (using nitric acid);
- precipitation of heavy metals under alkaline conditions and flocculation;
- filtration;
- ion exchange: the remaining heavy metal ions still dissolved in the lower ppm limit range are removed by means of a sodium ion exchanger (see Section 3.3.2.3.4.11);
- acidification with nitric acid to remove (hydrogen) carbonate (i.e. converted to CO_2).

As a result, the waste water fed into RO only contains sodium ions, ammonium ions, and nitrate ions.

It is not possible to remove ammonium ions during the pretreatment stage; they are concentrated together with the sodium nitrate in the RO. However, the ammonium ions accumulate in the exhaust air of the evaporator and are recycled for internal use via the NH_3 stripper (steam stripping) of the plant.

Multiple stage evaporation with adjacent crystallisation follows RO.

The NaNO$_3$ removed from the waste water is sold as crystalline NaNO$_3$ or, rarely, as a concentrated solution. The market for NaNO$_3$ is the fertiliser, chemical, glass and explosive/pyrotechnics industries, as well as for building materials, for the metal working industry and for the food sector. The usual market specifications can be met without problems.

An alternative treatment to the one described above is nitrification/denitrification (see Section 3.3.2.3.5.5). With such treatment, a reducing agent is needed. Because the pH increases during the reduction process, acid is added to decrease the pH: in essence, nitrate is substituted by the added acid ion, so the actual common salt load remains unchanged and will not decrease.

Achieved environmental benefits
Compared to nitrification/denitrification, the technique offers several environmental benefits including:

- avoiding sewerage sludge (bacterial mass) that should be properly disposed of;
- avoiding emissions of the greenhouse gas N$_2$O;
- returning sodium nitrate into the value added chain;
- savings of fresh water;
- reducing heavy metal and salt loads (chloride/sulphate) into the receiving water.

Cross-media effects
The cross-media effects include the use of energy (mainly for the RO and the downstream evaporation plant). The energy consumption of the NITREA$^{®}$ plant is about 950 000 kWh and 5 340 tonnes of steam per year.

While multi-stage evaporators require less heat to operate, they also necessitate higher investments than single-stage evaporators. Plant operators will have to determine individually their break-even point between investment and operating costs.

Operational data
An example for the abatement efficiencies associated with the removal and reuse of nitrate from waste water is given in Table 3.139.

Table 3.139: Example of environmental performance of the removal and reuse of nitrate from waste water

Parameters	Before installation of NITREA$^{®}$ (average for 2001 to 2005)	After installation of NITREA$^{®}$ (2007)	Abatement efficiency (%)
Discharged waste water	67 281 m^3	3 954 m^3	94
Nitrate	1 598 000 kg	260 kg	99.99
Ammonium (N-NH$_4$)	1 254 kg	49 kg	96
Sodium chloride	518 kg	0 kg	100
Heavy metals	21 kg	0.14 kg	99
NaNO$_3$ produced	0 kg	1 740 tonnes	NI
NB: NI = no information provided.			
Source: [137, LAWA 2008]			

Applicability
The technique is applicable in all plants with purely inorganic waste water after eliminating or removing all impurities (e.g. other ions, heavy metals) before RO treatment.

Economics
The NITREA® plant was put into operation in 2005. The total investment costs amounted to around EUR 9 000 000.

Operating costs amount to about EUR 580 per tonne of product A (to compare it with the previous costs for the waste water treatment; the costs have been compared with the most produced product of the plant: product A). The costs include the chemicals for waste water treatment, energy, labour costs, maintenance, quality control, depreciation, effluent charge but also savings of effluent charge, desalinated water and earnings from sodium nitrate. For comparative reasons, the previous waste water costs per tonne of product A were about EUR 1 400 in 2008.

For economic reasons, the technique may not be viable for processes with low influent concentrations of nitrate and denitrification might be an alternative (see Section 3.3.2.3.5.5) [227, CWW TWG 2009].

Driving force for implementation
The following are the main drivers for implementation:

* the regulatory drivers for emissions reduction;
* economic reasons.

Example plants
Clariant Produkte, Germany.

Reference literature
[137, LAWA 2008] [227, CWW TWG 2009]

3.4   Waste

3.4.1   Waste management

A wide range of wastes, including hazardous (according to legislation) wastes, are generated in chemical production plants, e.g. solvents (halogenated, non-halogenated), organic liquids, wash water, sludge from effluent treatment, salt solutions, process-related wastes (e.g. residues from distillation columns, tars and waxes, sludges in reactor vessels), off-specification products.

To prevent/minimise waste generation, the following hierarchy of measures applies in waste management:

1.waste prevention;
2.preparing/processing waste for reuse/recycling;
3.reuse/recycling of waste;
4.other recovery from waste, e.g. energy recovery;
5.disposal of waste without endangering human health and the environment.

Material flow analysis can be used to evaluate the production process of a chemical plant in the context of waste prevention/minimisation. Starting with the input raw materials, taking into account the energy efficiency of different production/recycling techniques as well as the overall impact of emissions, the plant operator is able to consider cross-media aspects in terms of waste prevention and recovery. At the end of the evaluation, and by means of adequate indicators, techno-economic decisions can be made by the plant operator in order to prevent/minimise waste generation.

Figure 3.48 shows a simplified decision-making scheme for an environmentally sound management of waste using the example of hazardous waste.
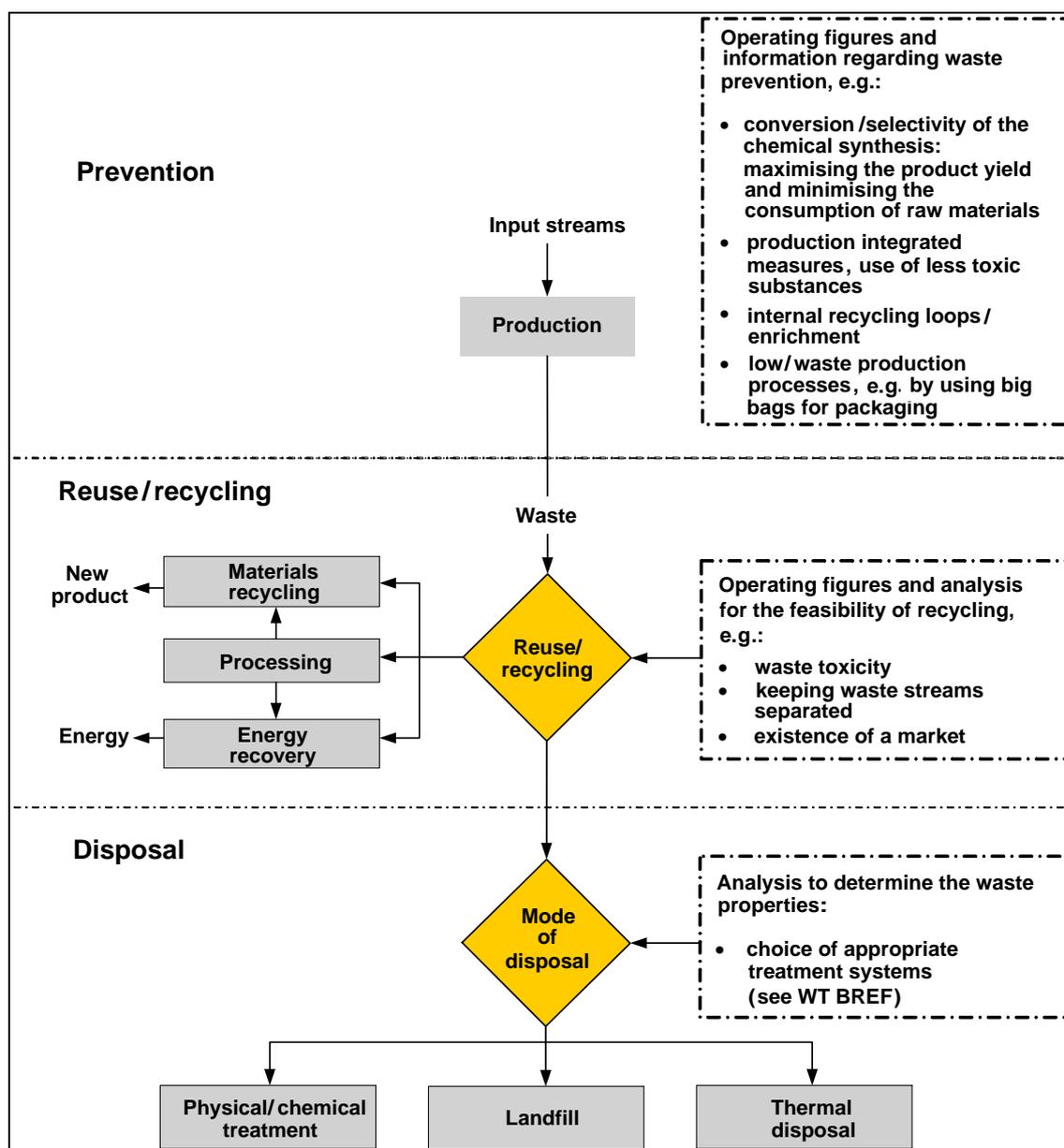
Figure 3.48: Simplified decision-making scheme for an environmentally sound management of waste using the example of hazardous waste

Chemical sites often offer opportunities to recycle waste in or from other installations whether chemical installations or non-chemical installations.

For more information on those treatments that can make a waste reusable or recoverable, the reader is advised to consult the Waste Treatment (WT) BREF [109, COM 2006]. Also, the sectorial chemical BREFs can provide information on the prevention and reuse/recycling of waste in the different sectors of the chemical industry.

3.4.2   Sludge treatment techniques

3.4.2.1   Overview

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 wt-% and 12 wt-% [1, Metcalf and Eddy 1991] and containing 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 for discharge or disposal, because:

- its content of pollutants offensive to air prevents its deposition;
- its content of pollutants offensive to water bodies prevents it from 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.

Mechanical, thermal and/or chemical techniques are used to reduce the sludge burden with the objective being to [164, Dewil et al. 2006]:

- reduce the quantity of waste sludge;
- achieve a better dewaterability of the sludge;
- provoke a release of soluble chemical oxygen demand (COD) from the sludge;
- destroy the filamentous microorganisms responsible for sludge bulking.

Such 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 3.4.2.2), such as:
  - gravity thickening,
  - centrifugal thickening,
  - flotation thickening (DAF),
  - gravity belt thickening,
  - rotary drum thickening;

- sludge stabilisation (see Section 3.4.2.3), such as:
  - chemical stabilisation (lime),
  - thermal stabilisation,
  - anaerobic digestion,
  - aerobic digestion,
  - dual sludge stabilisation;

- sludge conditioning (see Section 3.4.2.3), such as:
  - chemical conditioning,
  - thermal conditioning;

- sludge dewatering techniques (see Section 3.4.2.2), such as:
  - centrifugal dewatering,
  - belt filter presses,
  - filter presses;

- drying operations (not described in this document), such as:
  - rotary drying,
  - spray-drying,
  - flash drying,
  - evaporation;

- thermal sludge oxidation (outside the scope of this document), using techniques such as:
  - fluidised-bed incineration,
  - multiple-hearth drying/incineration,
  - wet air oxidation,
  - deep shaft oxidation,
  - incineration with other (e.g. solid) waste.

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. 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 sludge treatment technique.

Sludge originating from an industrial WWTP can under certain conditions be treated in a municipal WWTP (e.g. in Linz, Austria).

3.4.2.2 Thickening and dewatering

Description
Sludge thickening and sludge dewatering are operations to increase the solid content of sludge and remove part of the water fraction. Their benefit is a manifold (about fivefold 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 a dewatering technique), ideal for high solid capture, operated either as a solid bowl centrifuge or an imperforate basket centrifuge, illustrated in Figure 3.49;

NB: (a) Solid bowl centrifuge, (b) Imperforate basket centrifuge.
Source: [1, Metcalf and Eddy 1991]
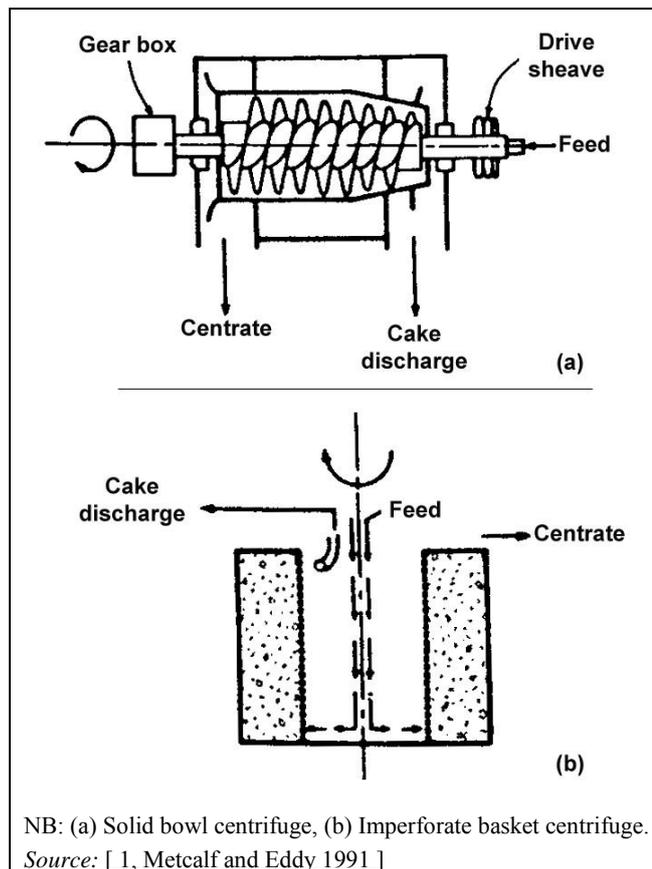
Figure 3.49: Centrifugal sludge thickener

- flotation thickening, using DAF equipment, as illustrated in Figure 3.50;
- 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;

Source: [1, Metcalf and Eddy 1991]
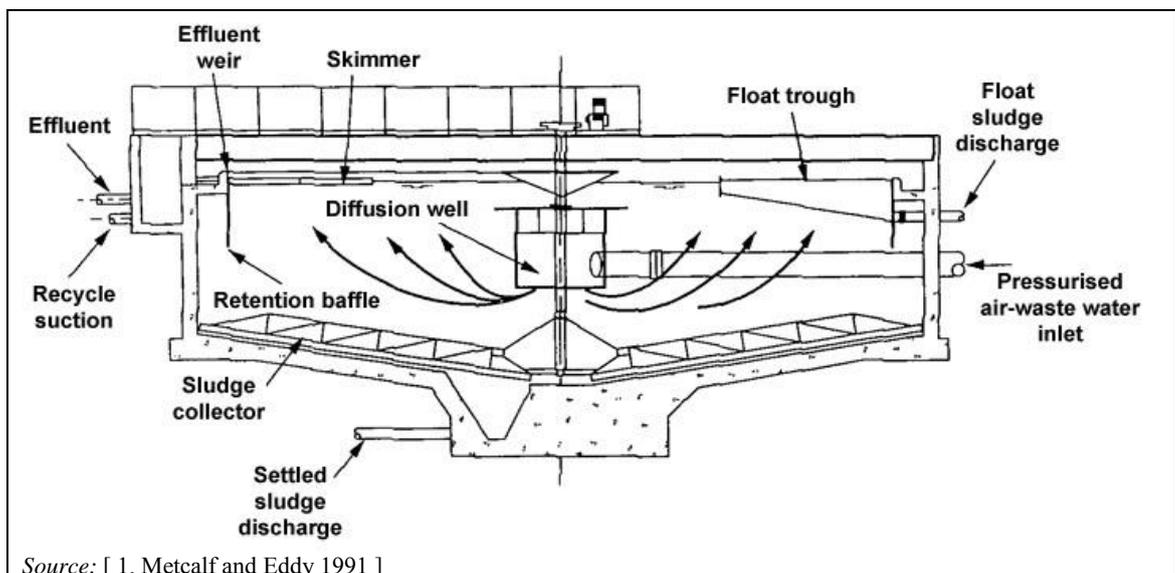
Figure 3.50: DAF thickener for waste activated sludge

- belt filter press dewatering, where the conditioned sludge is introduced into a gravity drainage section to thicken and separate from the water because of gravity, this operation is assisted by vacuum which simultaneously enhances drainage and reduces odour; then pressure is applied in a low-pressure sector, where the sludge is squeezed between opposing porous belts to release additional water (see Figure 3.51);

Source: [1, Metcalf and Eddy 1991].
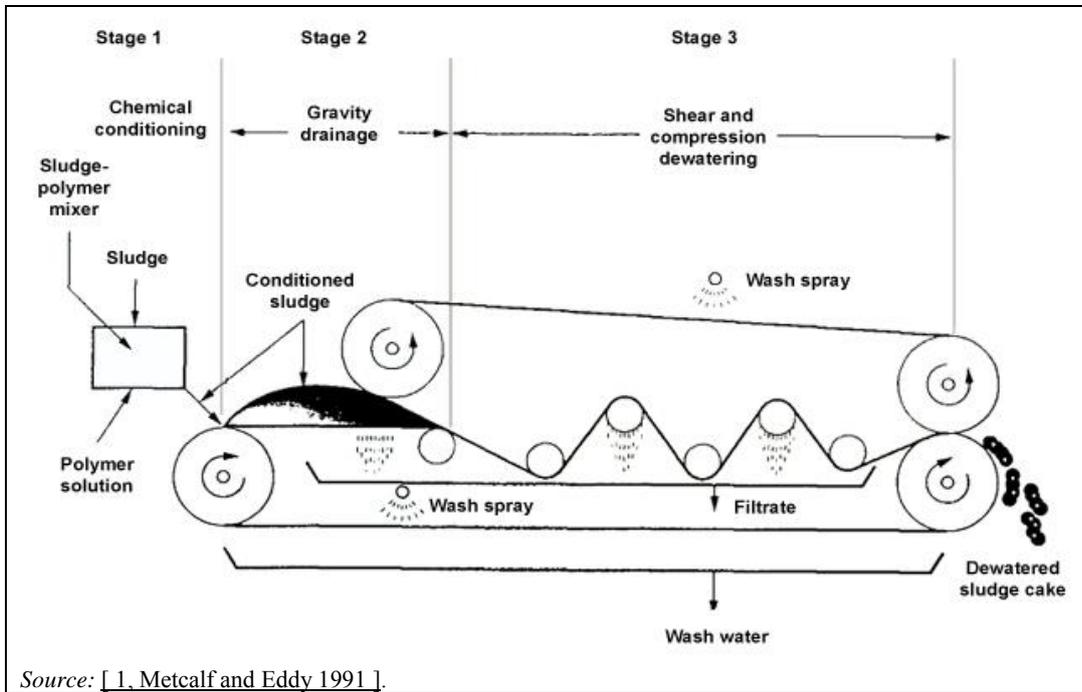
Figure 3.51: Belt filter press

- filter press dewatering, where the solid/liquid separation takes place at high pressure (0.7– 1.5 MPa) [1, Metcalf and Eddy 1991], the sludge is forced through a series of filter cloths to retain the particulates as filter cake and the filtrate is recycled to the waste water treatment plant (see Figure 3.52).

Source: [1, Metcalf and Eddy 1991].
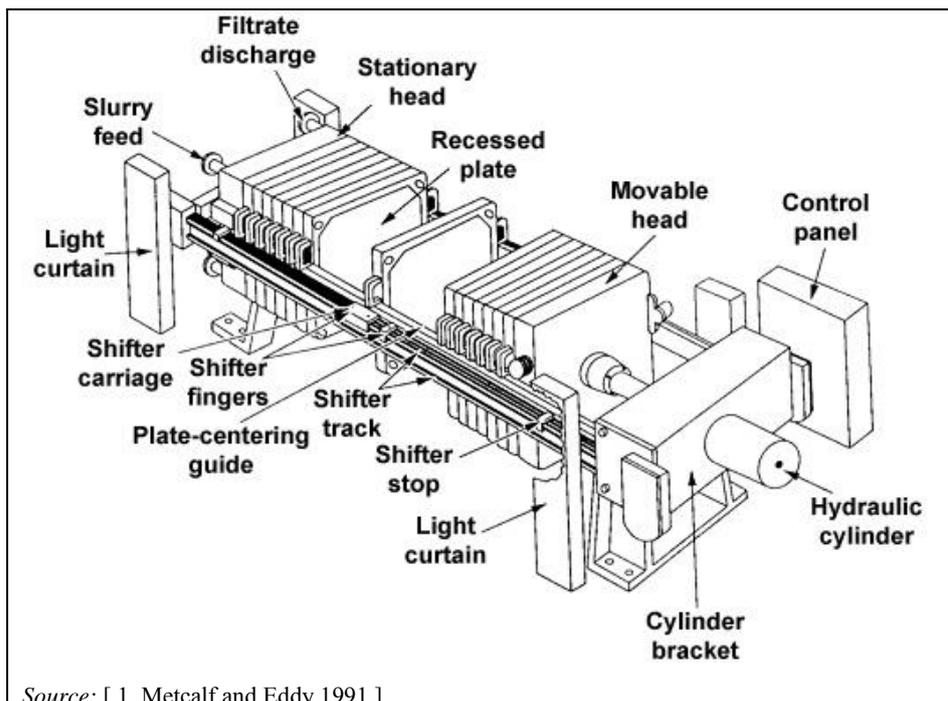
Figure 3.52: Fixed-volume recessed plate filter press

Achieved environmental benefits
Performance levels associated with sludge thickening and dewatering are given in Table 3.140.

Table 3.140: Performance levels associated with sludge thickening and dewatering

Technique	Sludge concentration (%)	Solids capture (%)	Comments
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])	NI	—
Rotary drum thickening	3–4 [1]	NI	—
	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]) [1, Metcalf and Eddy 1991]. ([2]) [63, VITO 2010]. NB: NI = no information provided.			

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 final treatment. The aqueous effluent (supernatant, filtrate) is recirculated back to the WWTP.

Noise and odour are controlled by enclosure and/or the housing of the equipment.

Consumables associated with sludge thickening and dewatering are given in Table 3.141.

Table 3.141: Consumables associated with sludge thickening and dewatering

Consumable	Amount	Comments
Conditioning chemicals	Polymer 0–4 kg/t dry matter ([1])	Solid bowl centrifuge
	Polymer 1–3 kg/t dry matter ([1])	Basket centrifuge
	Polymer 2–5 kg/t dry matter ([1])	DAF
	Polymer 3–7 kg/t dry matter ([1])	Gravity belt
Washing water	NI	For filter backwashing
Energy (kWh/m^3)	2–6	Solid bowl centrifuge
	2–3	Belt filter press
	4–5	Filter press
([1]) [1, Metcalf and Eddy 1991]. NB: NI = no information provided.		

Operational data
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 the filter cloth is concerned, the input needs to be controlled to prevent the entrance of oversized or otherwise critical solids.

Applicability
The various techniques and their application to sludge properties are given in Table 3.142.

Table 3.142: Applicability of sludge thickening and dewatering techniques depending on sludge properties

Gravity	• Untreated primary sludge • Waste activated sludge • Mixture of untreated primary sludge and waste activated sludge
Centrifugal	• Waste activated sludge, addition of flocculant and polymers necessary
DAF	• Waste activated sludge • Mixture of untreated primary sludge and waste activated sludge, addition of polymers necessary
Gravity belt	• Waste activated sludge, particularly to solids concentration of < 2 %
Rotary drum	• Waste activated sludge
Belt Filter Press	• All types of sludge, addition of flocculants and polymers necessary
Filter Press	• All types of sludge, flocculants and polymers needed • Used when low content of suspended solids in the filtrate is required

For all the techniques mentioned, the use of flocculants and polymers may be necessary.

Advantages and disadvantages are given in Table 3.143.

Table 3.143: Advantages and disadvantages associated with sludge thickening and dewatering

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 • Automatic adjustment to changes in sludge composition • Automatic start/stop • No operator required • No backflush water required	Centrifugal thickening • High consumption of energy per sludge unit dewatered • Produces highest cake solids concentration of the dewatering systems. Only the belt filter press usually results in a higher solid fraction than the centrifuge • 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) • Produces the lowest cake solids concentration of the dewatering systems
Gravity belt thickening • Good results for raw and digested sludge	NI
Rotary drum thickening • Low maintenance, energy and space requirements	NI
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
NB: NI = no information provided.	

Skilled personnel is required for the operation and maintenance of sludge thickening and dewatering techniques.

Economics
No information provided.

Driving force for implementation
The driving force for implementation is to decrease the volume of waste sludge in order to facilitate subsequent treatment operations as well as decrease the necessary size and capacity of treatment equipment.

Example plants
Many installations use this technique across Europe.

Reference literature
[1, Metcalf and Eddy 1991] [63, VITO 2010]

3.4.2.3 Stabilisation and conditioning

Description
Stabilisation techniques are [255, Ullmann's 2011]:

- 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 for 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 [1, Metcalf and Eddy 1991]; 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 digestion 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).

Achieved environmental benefits
Stabilisation of waste water sludge is a treatment operation to [255, Ullmann's 2011]:

- 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.

Cross-media effects
Chemical stabilisation and conditioning result in a considerable rise in the 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 [1, Metcalf and Eddy 1991].

The necessary amount of lime for sludge stabilisation is detailed in Table 3.144, the amount of polymer for sludge conditioning in Table 3.145.

Table 3.144: Typical lime dosages for stabilising liquid sludge

Sludge	Solids concentration (%)	Lime dosage ([1]) (kg lime/kg dry matter)
Primary sludge	3–6	120–340
Waste activated sludge	1–5	420–860
Aerobically digested mixed sludge	6–7	280–500
Septage sludge (i.e. from septic tank)	1–4.5	180–1020
([1]) Amount of lime required to maintain a pH of 12 for 30 minutes.		
Source: [1, Metcalf and Eddy 1991]		

Table 3.145: Typical levels of polymer addition for various types of sludge and for various methods of dewatering

Sludge	kg dry polymer/t dry matter		
	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	NI
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 aerated waste activated sludge	1.5–8.5	1.5–8.5	2–5
Aerobically digested primary sludge and aerated waste activated sludge	7.5–10	2–8	NI
NB: NI = no information provided.			
Source: [1, Metcalf and Eddy 1991]			

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 boilers and internal combustion engines.

Thermal stabilising and conditioning is an energy-intensive process which has to be assessed on its merits given particular circumstances. During operation, odorous substances are generated which can be released and would have to be abated accordingly.

Applicability
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, such as:

- available of 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 are given in Table 3.146.

Table 3.146: Advantages and disadvantages associated with stabilisation and conditioning of sludge

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 solids increase (except polymer conditioning)
Thermal stabilisation and conditioning •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 investment 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 investment costs than with anaerobic digestion	Aerobic digestion •High energy needs 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 without the use of additional chemicals •Because of long residence time, there is an efficient mineralisation of the sludge	Anaerobic digestion •Large space requirements are an issue for small sites

Economics
No information provided.

Driving force for implementation
The driving force for implementation is to reduce odorous emissions and improve subsequent treatment operations.

Example plants
Stabilisation and conditioning of sludge is widely used in Europe.

Reference literature
[1, Metcalf and Eddy 1991] [255, Ullmann's 2011]

3.5 Emissions to air

3.5.1 Individual waste gas treatment techniques

3.5.1.1 Overview

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 referred to in Section 1.6.3.3, is illustrated in Figure 3.53.
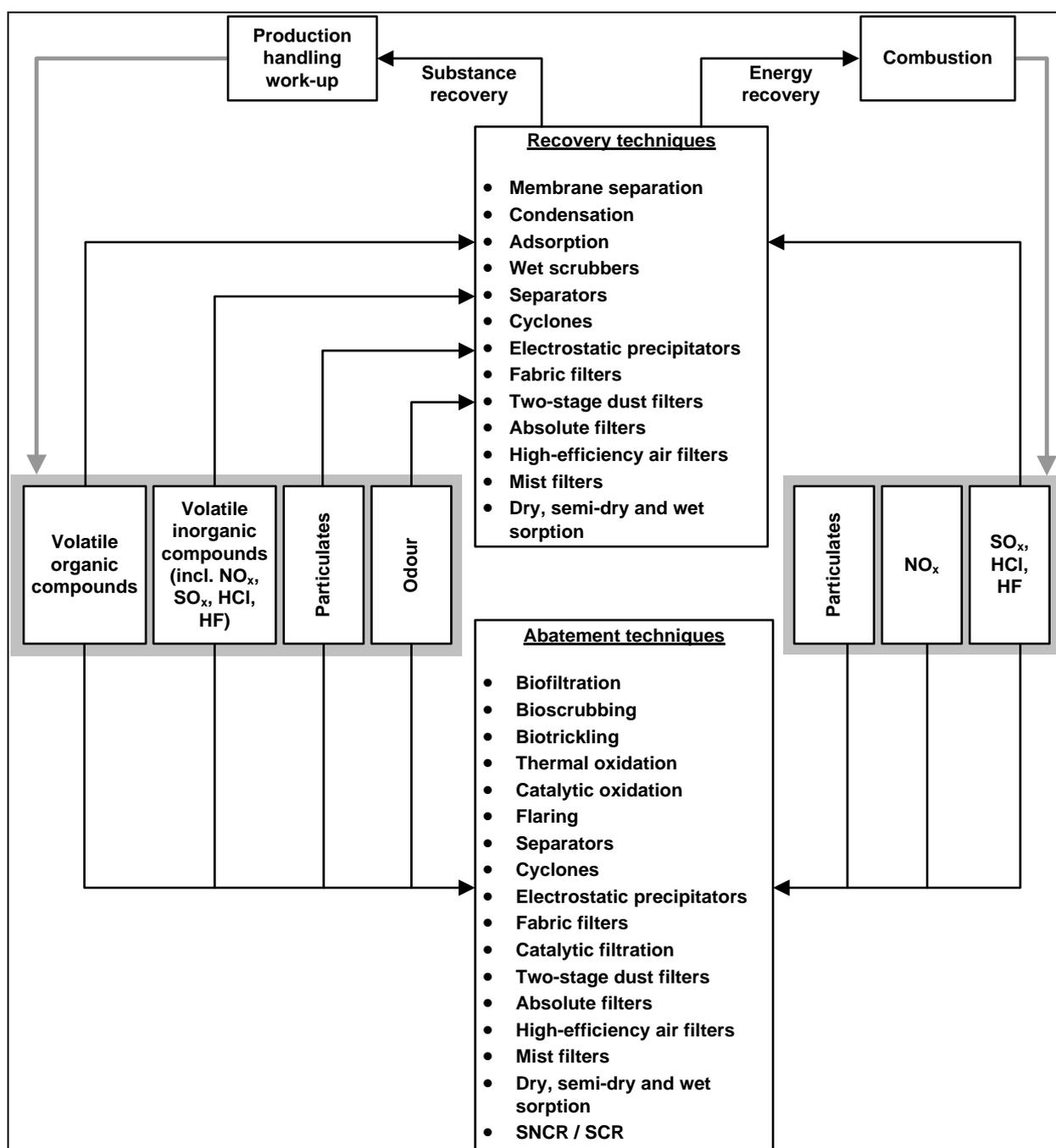
Figure 3.53: Range of waste gas end-of-pipe treatment techniques in relation to type of contaminants

The sources of waste gases to be treated are:

- low- to medium-temperature processes (< 300 °C), such as production, handling or work-up processes, with the main contaminants being:
  - volatile organic compounds, such as solvents;
  - inorganic compounds, such as hydrogen halides, hydrogen sulphide, ammonia, and carbon monoxide;
  - particulates in the form of dust;
  - odour;
- high-temperature processes (> 850 °C) (e.g. incineration processes), with the main contaminants being:
  - particulate matter (PM) in the form of ashes and dust, which might contain soot and metal oxides;
  - flue-gases such as carbon monoxide, hydrogen halides (e.g. HCl, HF), sulphur-oxygen compounds (SO_X) and nitrogen-oxygen compounds (NO_X);
  - odour.

Arising waste gases are treated by techniques by which the waste gas content is recovered and either recycled to the original process or used in another process as a raw material or energy carrier, or the contaminants are abated.

Compounds for which recovery is economically feasible (depending on the compounds' concentration in the waste gas, waste gas flow and variations in concentration and flow) include:

- VOCs, recovered from solvent vapours or vapours of low-boiling products;
- VOCs used as an energy carrier in incinerators/oxidisers or boilers;
- hydrogen chloride, to produce hydrochloric acid;
- ammonia to recycle into the production process;
- sulphur dioxide, transferred into sulphuric acid, sulphur or gypsum;
- dust which contains higher amounts of solid raw products or end-products.

The treatment techniques are – as per Figure 3.53 – classified as:

- recovery/abatement techniques for VOCs and inorganic compounds including:
  - membrane separation (see Section 3.5.1.2.1);
  - condensation and cryogenic condensation (see Section 3.5.1.2.2);
  - adsorption (see Section 3.5.1.2.3);
  - wet scrubbing (see Section 3.5.1.2.4);

- abatement techniques for VOCs and inorganic compounds including:
  - biofiltration (see Section 3.5.1.3.1);
  - bioscrubbing (see Section 3.5.1.3.2);
  - biotrickling (see Section 3.5.1.3.3);
  - moving-bed trickling (see Section 3.5.1.3.4);
  - thermal oxidation (see Section 3.5.1.3.5);
  - catalytic oxidation (see Section 3.5.1.3.6);
  - ionisation (see Section 3.5.1.3.7);
  - photo/UV oxidation (see Section 3.5.1.3.8);

- recovery and abatement techniques for particulates, using:
  - settling chamber/gravitational separator (see Section 3.5.1.4.2);
  - cyclone (see Section 3.5.1.4.3);
  - electrostatic precipitator (see Section 3.5.1.4.4);
  - wet dust scrubber (see Section 3.5.1.4.5);
  - fabric filter (see Section 3.5.1.4.6);

- ◦ ceramic and metal filter (see Section 3.5.1.4.7);
- ◦ catalytic filter (see Section 3.5.1.4.8);
- ◦ two-stage dust filter (see Section 3.5.1.4.9);
- ◦ absolute filter (see Section 3.5.1.4.10);
- ◦ high-efficiency air filter (HEAF) (see Section 3.5.1.4.11);
- ◦ mist filter (see Section 3.5.1.4.12);

- • recovery and abatement techniques for combustion waste gases:
  - ◦ dry sorbent injection (see Section 3.5.1.5.2);
  - ◦ semi-dry sorbent injection (see Section 3.5.1.5.2);
  - ◦ wet sorbent injection (see Section 3.5.1.5.2);
  - ◦ selective non-catalytic reduction of NO_X (SNCR) (see Section 3.5.1.5.3);
  - ◦ selective catalytic reduction of NO_X (SCR) (see Section 3.5.1.5.3);
  - ◦ non-selective catalytic reduction of NO_X and N_2O (see Section 3.5.1.5.4);

- • flaring for safety reasons or non-routine operational conditions (see Section 3.5.1.6).

Most of the recovery/abatement techniques mentioned above can be used to prevent or abate/minimise emissions of odorous substances (see Section 3.5.5).

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 prefilter, or they are used as a final polishing step. Others can be used as both individual or secondary technology. Examples are given in the sections 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 sections below.

Table 3.147 gives an overview of the waste gas end-of-pipe treatment techniques described in the following sections with respect to the pollutants to be recovered or abated.

Table 3.147: Overview of the waste gas treatment techniques with respect to the pollutants to be abated

Working principle	Technique	Dry dust	Wet dust	Droplets/aerosols	VOC	SO₂	H₂S	NOₓ	NH₃	HCl/HF	Heavy metals	Dioxins/furans	Section in this document
Gravitational separation	Settling chamber/gravitational separator	♦	♦	✦									3.5.1.4.2
	Cyclones	♦	♦										3.5.1.4.3
Dust scrubbing	Wet dust scrubber	♦	♦		✦	✦	✦		✦	✦			3.5.1.4.5
	Spray tower	♦	♦		✦	✦	✦		✦	✦			3.5.1.4.5
	Venturi scrubber	♦	♦		✦	✦	✦		✦	✦			3.5.1.4.5
Filtration	Dry ESP	♦	♦										3.5.1.4.4
	Wet ESP	♦	♦										3.5.1.4.4
	Fabric filter	♦											3.5.1.3.5
	Ceramic and metal filter	♦				✦		✦		✦			3.5.1.4.7
	Catalytic filtration	♦			✦					✦		♦	3.5.1.4.8
	Two-stage dust filter	♦											3.5.1.4.9
	Absolute filter (HEPA)	♦									♦		3.5.1.4.10
	High-efficiency air filter (HEAF)			♦									3.5.1.4.11
	Mist filter		♦	♦									3.5.1.4.12
Condensation	Condenser				♦				♦				3.5.1.2.2
	Cryogenic condensation				♦								3.5.1.2.2
Adsorption	Adsorption (general)				♦							♦	3.5.1.2.3
	Adsorption (active coal)				♦		♦				♦	♦	3.5.1.2.3
	Adsorption (zeolites)				♦				♦				3.5.1.2.3
	Adsorption (polymeric)				♦								3.5.1.2.3
	Dry sorbent injection					♦				✦			3.5.1.5.2
	Semi-dry (or semi-wet) sorbent injection					♦				✦			3.5.1.5.2
	Wet sorbent injection					♦				✦			3.5.1.5.2
Absorption	Wet gas scrubber	✦	✦		♦	♦			♦	♦			3.5.1.2.4
	Acid gas scrubber	✦	✦		♦				♦				3.5.1.2.4
	Alkaline gas scrubber	✦	✦		♦	♦	♦			♦			3.5.1.2.4
Bioprocesses	Biofiltration				♦		✦		♦				3.5.1.3.1
	Bioscrubbing				♦		✦		♦				3.5.1.3.2

Working principle	Technique	Removed pollutants											Section in this document
		Dry dust	Wet dust	Droplets/ aerosols	VOC	SO_2	H_2S	NO_X	NH_3	HCl/HF	Heavy metals	Dioxins/ furans	
	Biotrickling				◆		✦		◆				3.5.1.3.3
	Moving-bed trickling filter				◆		✦						3.5.1.3.4
Thermal oxidation	Thermal oxidiser				◆								3.5.1.3.5
	Catalytic oxidiser				◆								3.5.1.3.6
	Flaring				◆								3.5.1.6
Cold oxidation	Ionisation				◆								3.5.1.3.7
	Photo/UV oxidation				◆		◆		◆				3.5.1.3.8
Chemical reduction	Selective non-catalytic reduction (SNCR)							◆					3.5.1.5.3
	Selective catalytic reduction (SCR)							◆					3.5.1.5.3
	Non-selective catalytic reduction (NSCR)				✦			◆					3.5.1.5.4
Other techniques	Membrane separation				◆								3.5.1.2.1
	Recovery of NO_X from waste gas							◆					3.5.1.5.5

NB: ◆ = the primary goal of the technique is the removal of (a) specific pollutant(s). ✦ = the primary goal of the technique is not the removal of specific pollutants, but these pollutants are also, in some cases partially, removed using the technique.

3.5.1.2   Recovery/abatement techniques for VOCs and inorganic compounds

3.5.1.2.1   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 [14, Hydrocarbon Processing 1998]). The waste gas stream is compressed and passed over the membrane. The enriched permeate can be recovered by methods such as condensation (see Section 3.5.1.2.2) or adsorption (see Section 3.5.1.2.3), or it can be abated, e.g. by catalytic oxidation (see Section 3.5.1.3.6). The process is most appropriate for higher vapour concentrations. Additional treatment is, in most cases, needed to achieve concentration levels low enough to discharge [20, HMIP 1994].

Membrane separators are designed as modules, e.g. as capillary modules (see Figure 3.54), manufactured as a polymer layer.

Source: [9, BASF 1999]
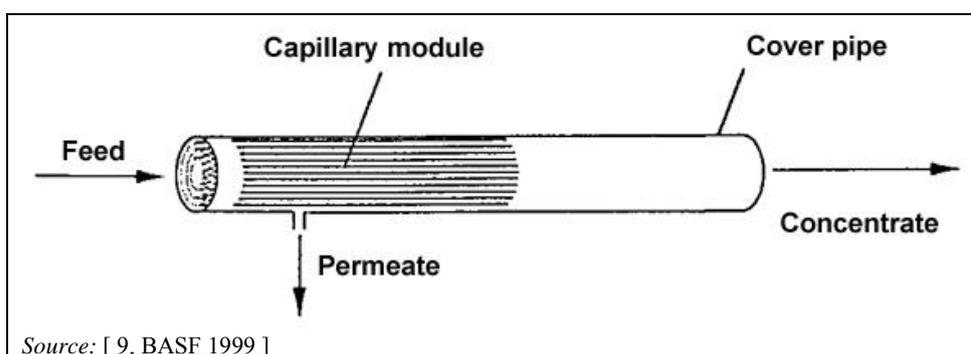
Figure 3.54: Typical membrane capillary module

The configuration of the membrane varies depending on the supplier (e.g. flat membranes, hollow fibre membranes). The material of the membranes can also vary (e.g. organic and inorganic membranes). The choice of the membrane system is made based on the characteristics of the waste gas to be treated (e.g. temperature, pressure) [176, Schenk et al. 2009].

A membrane separation system consists of (see Figure 3.55):

- the membrane modules;
- a compressor;
- a recovery unit (e.g. condenser, adsorber);
- vents and ducts;
- possibly a second stage for further treatment.
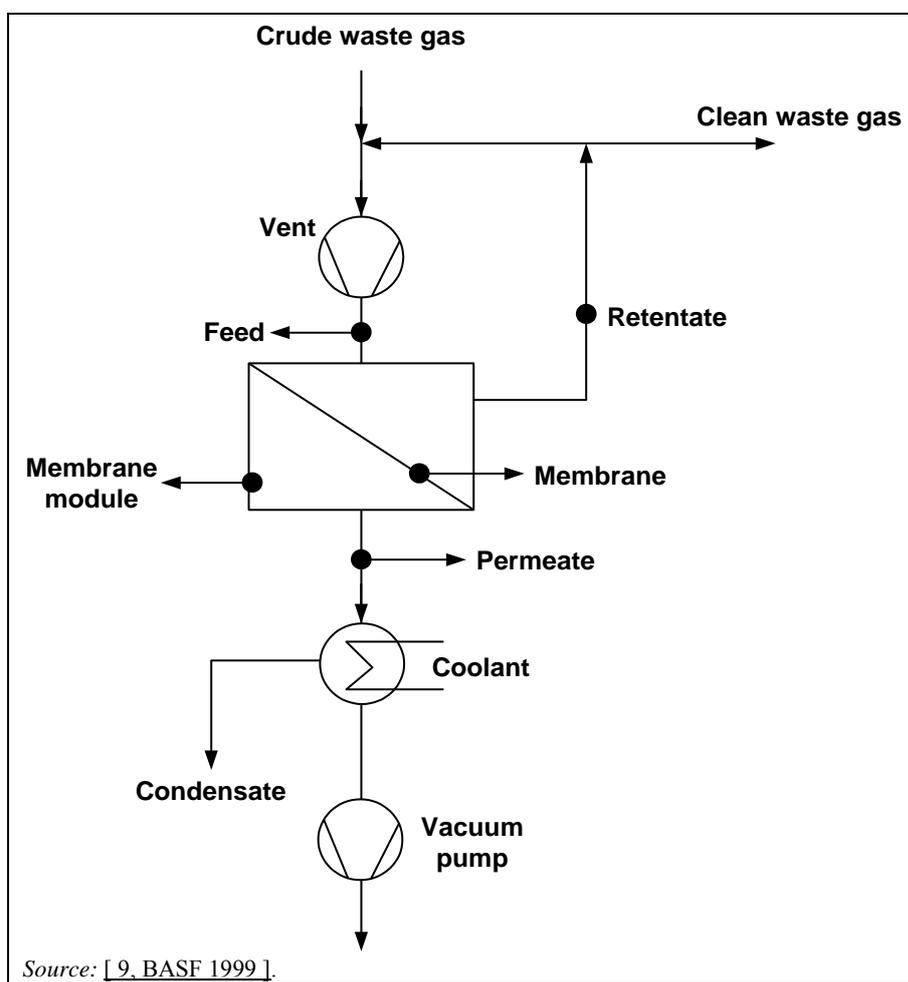
Figure 3.55: Common membrane separation system

To create the necessary pressure difference between the feed and permeate sides of the membrane (0.1–1 MPa), the system works by means of excess pressure on the feed side, by vacuum (about 0.2 kPa) on the permeate side or by both [9, BASF 1999].

During the rise of vapour concentration within the membrane unit, the concentration level can climb from lower to higher than the explosive limit and thus develop an explosive mixture. Safety is therefore a crucial issue that needs to be taken into account.

An example of a membrane separation process used as a vapour recovery unit (VRU) is illustrated in Figure 3.56. Here a second treatment stage (PSA, see Section 3.5.1.2.3) improves the emission, according to the defined emissions requirements. This technology is well-suited to systems with large vapour volumes because of the use of a compressor at the inlet to the membrane unit [113, COM 2006]. Where the upstream vapour volume is small, e.g. road tanker loading, then it is common practice to install a variable volume vapour-holding tank at the inlet to the VRU.

Source: [14, Hydrocarbon Processing 1998]
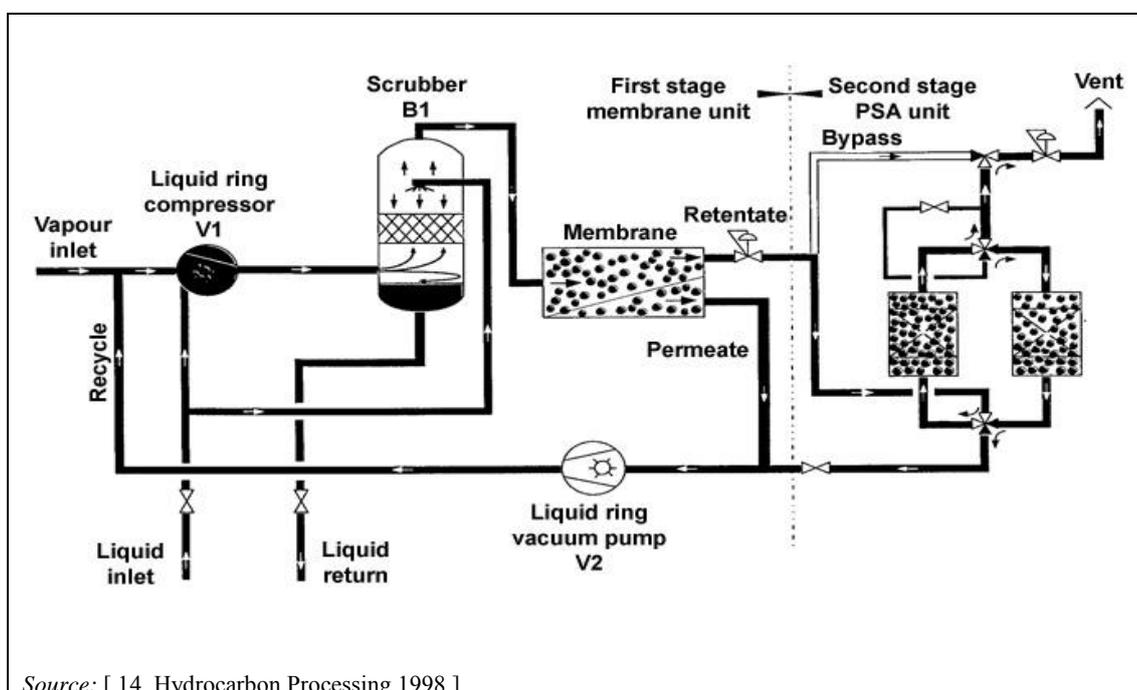
Figure 3.56: Application of a membrane separation process used as a vapour recovery unit (VRU)

Achieved environmental benefits
Achieved environmental benefits associated with membrane separation are given in Table 3.148.

Table 3.148: Abatement efficiencies and emission levels associated with membrane separation

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm^3)
VOCs	Up to 99.9	150–300

([1]) Efficiency depends on the specific plant configuration and operating conditions; the performances indicated are based upon half-hourly averages.
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given have to be used with extreme caution for permitting.
Source: [176, Schenk et al. 2009]

Cross-media effects
Consumables associated with membrane separation are given in Table 3.149.

Table 3.149: Consumables associated with membrane separation

Consumable	Amount	Comments
Membrane material	NI	Membranes have to be replaced periodically, although they theoretically have a very long lifespan. The guarantee on the lifespan of membranes is often five years ([1])
Cooling medium	NI	—
Energy (kWh/1 000 Nm^3)	250 ([1])–300 ([1])	Electric energy for fan included
Pressure drop (MPa)	0.1–1 ([2])	—

([1]) [176, Schenk et al. 2009].
([2]) [9, BASF 1999].
NB: NI = no information provided.

Membrane separation requires a double set of vapour-moving equipment, e.g. a liquid ring vacuum pump and a compressor, so there is potential for high energy usage.

Membrane separation is frequently used as a concentration step to facilitate further recovery or treatment, such as:

- enrichment of VOCs in the gas phase which 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 which 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 a stack or to a subsequent waste gas treatment step, such as adsorption or incineration.

Operational data
Design and maintenance [176, Schenk et al. 2009]
The design of a membrane separation system is based on the waste gas flow to be treated, the concentration and type of pollutants in the waste gas, the type of membrane (surface pressure) used, and the degree of material recovery. Simple mechanical principle and little maintenance are required. LEL values should be taken into account at the design stage to prevent the risk of explosion.

Monitoring
The efficiency of the membrane separation system is determined by monitoring the concentration of VOCs 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 sides of the membrane. For safety reasons, the VOC/oxygen ratio should be carefully controlled (for explosion risk).

Applicability
Membrane separation is applied in the chemical industry, the petrochemical industry, and the pharmaceutical industry, etc. to recover solvent vapours from the waste gas. Examples are [14, Hydrocarbon Processing 1998] the recovery of:

- olefin monomers from polyolefin resin degassing streams;
- vinyl chloride from PVC manufacturing;
- solvent and hydrocarbon vapours from tank filling.

Recoverable compounds include alkanes, olefins, aromatics, chlorinated hydrocarbons, alcohols, ethers, ketones and esters.

Application limits and restrictions are given in Table 3.150.

Table 3.150: Application limits and restrictions associated with membrane separation

Issue	Limits/restrictions
Waste gas flow (Nm^3/h)	Dependent on membrane surface area, capacities of 2 100–3 000 Nm^3/h are known
Temperature	Ambient temperature, dependent on membrane material
Pressure (bar)	Dependent on membrane material ~ 3.5 (up to 100 with inorganic membranes)
Pressure drop (bar)	1–10
Dust content	Very low; dust can damage the membrane surface thus very low dust concentrations have to be achieved in advance
VOC concentration	From dilute to concentrated streams (containing up to 90 % VOCs); high concentrations can be treated
Source: [176, Schenk et al. 2009].	

Advantages and disadvantages are given in Table 3.151.

Table 3.151: Advantages and disadvantages associated with membrane separation

Advantages	Disadvantages
• The reuse of raw material is possible • The operation in itself is simple; little maintenance is required • No waste generated by the process	• Subsequent work-up and/or treatment step is necessary • Explosion risk • Only suitable for large – fixed – upstream vapour volumes because of potential safety issues with inlet compressor

Economics
Economics associated with membrane separation are given in Table 3.152.

Table 3.152: Economics associated with membrane separation

Type of costs	Costs	Comments
Investment costs	EUR 345 000	For a 200 Nm^3/h treatment system
Operating costs:	< EUR 50	Per 1 000 Nm^3/h
Labour	EUR 1 500/yr	4 days per year
Utilities	EUR 60 000/yr per 1 000 Nm^3/h	—
Cost-determining parameters	Gas flow, technical lifespan of membrane, required degree of material recovery, required final concentration	
Benefits	Potential material recovery	
NB: NI = no information provided.		
Source: [176, Schenk et al. 2009].		

Cost-relevant parameters are the waste gas flow rate and the technical service life of the membrane. Revenue is the recovered VOCs.

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 [14, Hydrocarbon Processing 1998]. 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 than a one-step membrane separation.

Driving force for implementation
The driving force for implementation is material recovery.

Example plants
The technique is reported to be widely used in the (petro)chemical industry sector as well as in other sectors such as refineries.

Reference literature
[9, BASF 1999] [14, Hydrocarbon Processing 1998] [20, HMIP 1994] [113, COM 2006] [176, Schenk et al. 2009]

3.5.1.2.2 Condensation and cryogenic 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 and include:

- coolant condensation, for a condensation temperature down to about 25 °C;
- refrigerant condensation, for a condensation temperature down to about 2 °C;
- brine condensation, for a condensation temperature down to about -10 °C;
- ammonia brine condensation, for a condensation temperature down to about -40 °C (one-stage) or -60 °C (two-stage);
- cryogenic condensation, for a condensation temperature down to about -120 °C, in practice often operated between -40 °C and -80 °C in the condensation device;
- closed-cycle inert gas condensation.

Condensation is carried out by means of direct cooling (i.e. contact between gas and cooling liquid) or indirect cooling (i.e. cooling via a heat exchanger) (see Figure 3.57). 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 [12, ETBPP 1996].


Source: [176, Schenk et al. 2009]
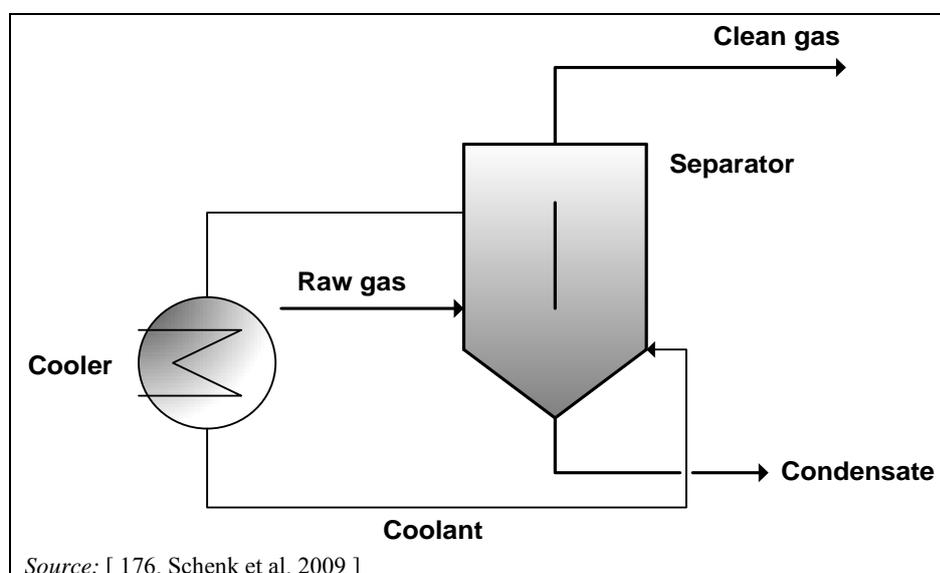
Figure 3.57: Condenser system

The design and operation of condensers are highly dependent on the cooling medium used in the process. An example includes a device for liquid-cooled (i.e. not cryogenic) condensation which is operated with a conventional shell-and-tube heat exchanger or a spiral heat exchanger.

Conventional shell-and-tube heat exchanger
[12, ETBPP 1996] The conventional shell-and-tube heat exchanger is either water-cooled or air-cooled. The condensation efficiency can be improved by a two-stage operation, using water in the first stage and refrigerated liquid (water, brine, etc.) as a cooling medium in the second stage. Such a two-stage system consists of (see Figure 3.58):

- the recuperator, using the cold purified gas stream as a chilling agent;
- the precooler 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 the removal of the remaining VOCs from the gas stream by a different technique, such as adsorption (see Section 3.5.1.2.3).

To minimise fog formation, a series of condensers can be used, as well as a demister supported by gas velocity reduction in the condenser.

Source: [12, ETBPP 1996]
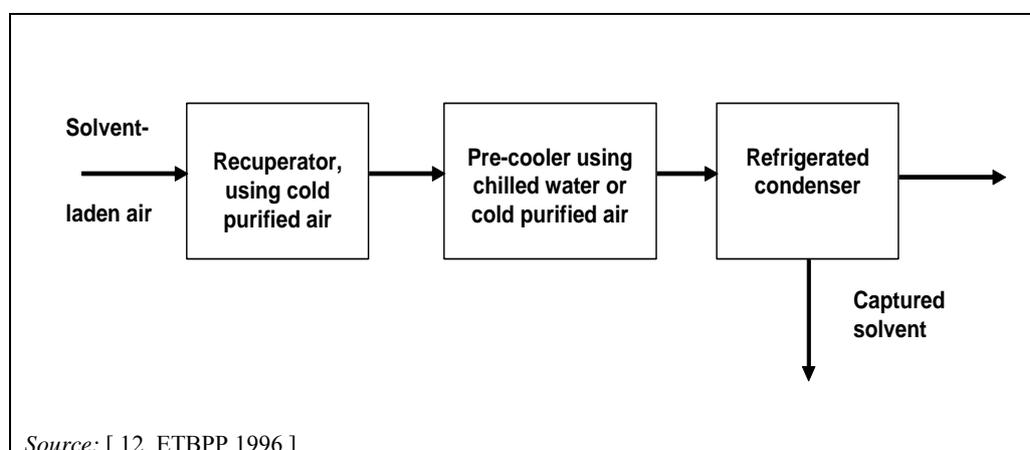
Figure 3.58: Two-stage condensation system

Spiral heat exchanger
[12, ETBPP 1996] The spiral heat exchanger basically consists 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 foul, which requires flushing programmes and/or cooling water treatment.

In the presence of acidic or alkaline compounds, a recirculation system which contains acid or an alkali dosage might be considered.

Cryogenic condensation
Cryogenic condensation is operated using the vaporisation of liquid nitrogen as a coolant medium to condense VOC vapour at the condenser surface. The evaporated nitrogen is used to provide inert blanketing.

The cryogenic condensation system consists of:

- the precondenser, 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 variant is condensation under inert atmosphere, i.e. nitrogen, to enable the gas stream to contain higher concentrations of VOCs. Examples of cryogenic condensation are given in Figure 3.59 and Figure 3.60.

Source: [12, ETBPP 1996]
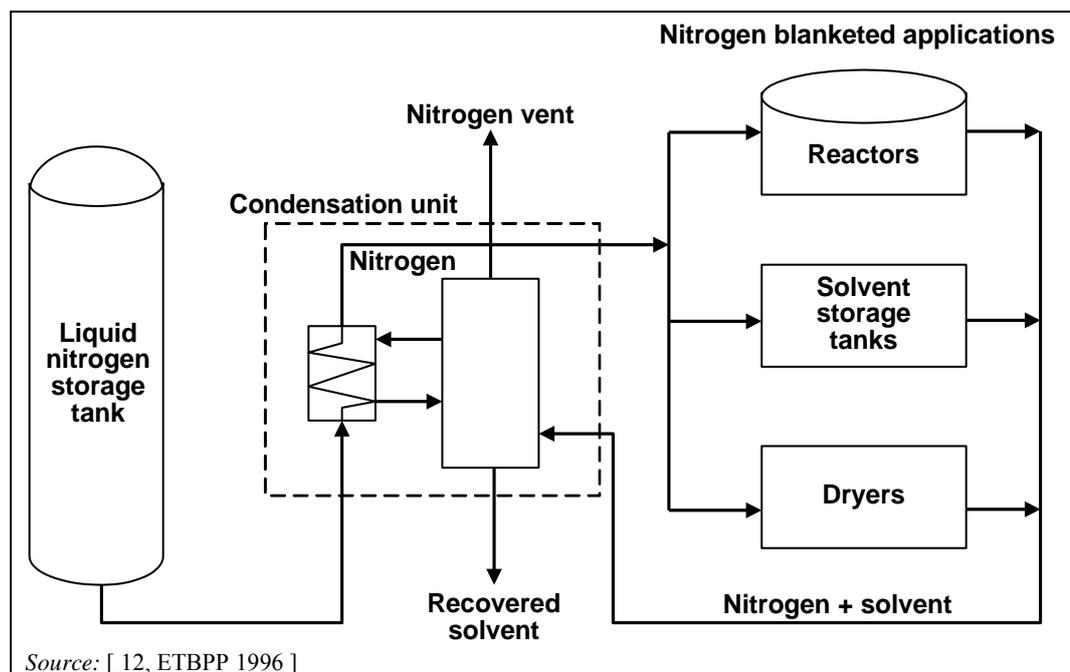
Figure 3.59: Cryogenic condensation integral recovery system with a typical nitrogen blanketing operation
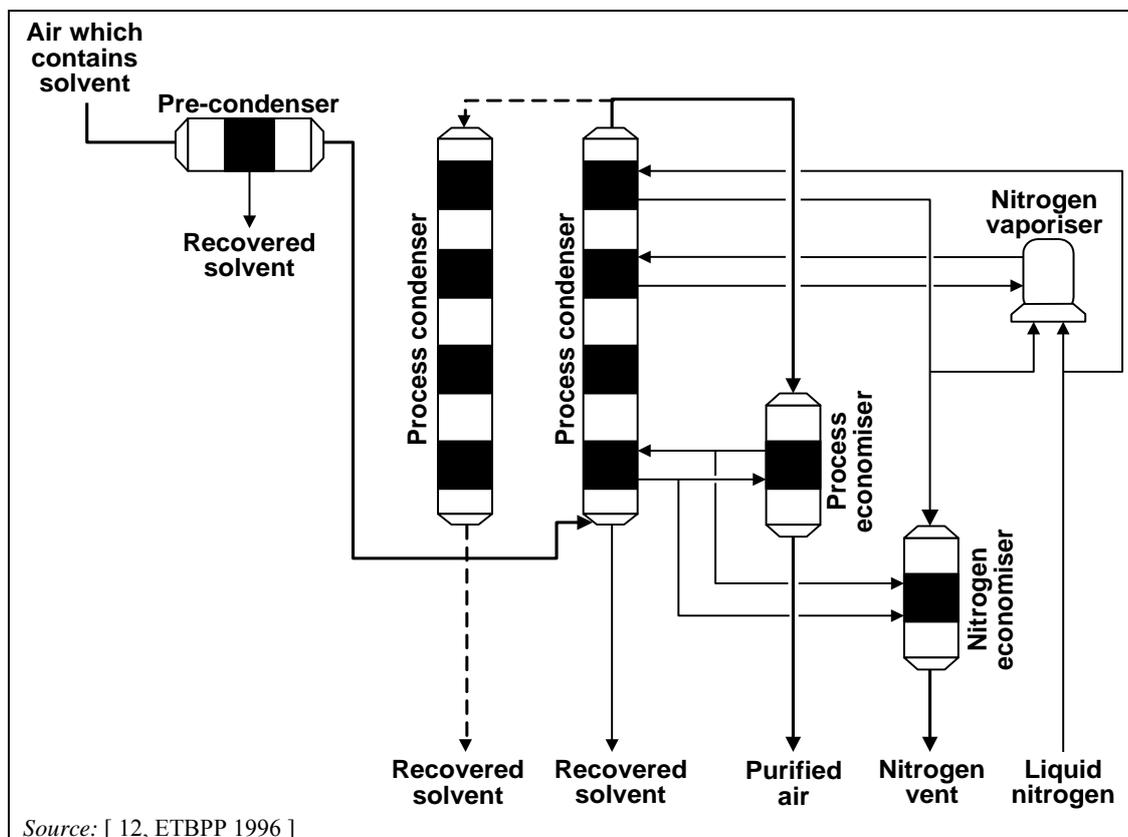
Figure 3.60: Cryogenic recovery system under inert atmosphere

Closed-cycle inert gas condensation
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 [12, ETBPP 1996].

A typical closed-cycle inert gas condensation system consists of (see Figure 3.61):

* the heat exchanger, precooling the gas stream;
* the main condenser, mechanically refrigerated to as low as -40 ºC;
* the solvent separator and the nitrogen supply.

Source: [12, ETBPP 1996]
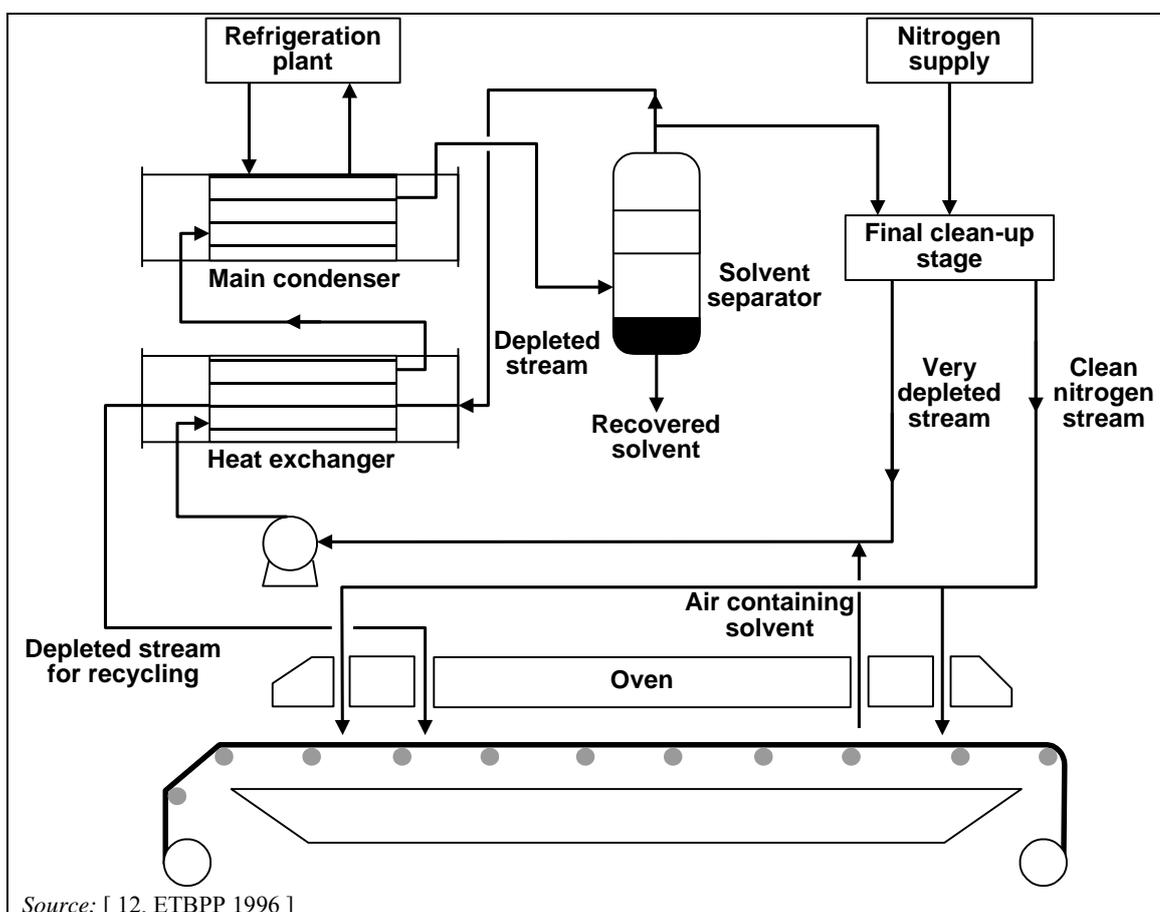
Figure 3.61: Typical closed-cycle inert gas condensation system

Achieved environmental benefits
Achieved environmental benefits associated with condensation and cryogenic condensation are given in Table 3.153 and Table 3.154.

Coolant condensation
Abatement efficiencies and emission levels associated with condensation are given in Table 3.153.

Table 3.153: Abatement efficiencies and emission levels associated with condensation

Pollutant	Abatement efficiency (%)	Emission level (mg/Nm^3)	Comments
Odour	60–90 ([1])	NI	—
Ammonia	80–90 ([1])	NI	Initially 200–1 000 mg/Nm^3
Dust	80–90 ([1])	NI	—
([1]) Depending on the specific configuration and operational conditions. NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].			

Cryogenic condensation
Abatement efficiencies and emission levels associated with cryogenic condensation are given in Table 3.154.

Table 3.154: Abatement efficiencies and emission levels associated with cryogenic condensation

Pollutant	Abatement efficiency (%)	Emission level (mg/Nm^3)	Comments
Toluene	NI	< 100 ([1])	At -65 °C, Initially 20–1 000 g/Nm^3
Methyl ethyl ketone	NI	< 150 ([1])	At -75 °C, Initially 20–1 000 g/Nm^3
Acetone	NI	< 150 ([1])	At -86 °C, Initially 20–1 000 g/Nm^3
Methanol	NI	< 150 ([1])	At -60 °C, Initially 20–1 000 g/Nm^3
Dichloromethane	NI	< 20 ([2])	—
VOC	> 99 ([2])	< 150 ([2])	Initially up to 1 000 g/Nm^3
([1]) [11, InfoMil 1999].			
([2]) Efficiency depends on the specific configuration and operational conditions; the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].			
NB: NI = no information provided.			

Cross-media effects

Consumables associated with condensation and cryogenic condensation are given in Table 3.155 and Table 3.156.

Coolant condensation

Table 3.155: Consumables associated with condensation

Consumable	Amount	Comments
Cooling medium (air, water, brine, ammonia-brine)	NI	Highly dependent on individual application
Energy (kWh/1 000 Nm^3)	NI	Vents, pumps, cooling facilities
Pressure drop (kPa)	0.1–0.2 ([1])	—
Corrosion inhibitors	NI	—
Biocides	NI	To prevent growth of microorganisms
([1]) [11, InfoMil 1999].		
NB: NI = no information provided.		

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: 200–1 000 mg/l COD;
- condensation of ammonia/amines: 400–2 000 mg/l Kjeldahl-N.

Cryogenic condensation

Table 3.156: Consumables associated with cryogenic condensation

Consumable	Amount	Comments
Nitrogen as cooling medium	10–15 kg/kW cooling ([1, 2])	Depends on plant design, solvent type, etc.
Energy (kWh/1 000 Nm^3)	70 ([2])	If cooling takes place by a compression cooling system. Dependent on the cooling system and the damping temperature.
Pressure drop (kPa)	2–5 ([3])	─
([1]) [12, ETBPP 1996]. ([2]) [176, Schenk et al. 2009]. ([3]) [11, InfoMil 1999]. NB: NI = no information provided.		

Further consumables are:

- steam as a 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 reused, processed or disposed of as liquid waste.

The consumption of liquid nitrogen is divided into:

- standby processing (to maintain the temperature);
- the cooling of the incoming gas stream for condensation.

There are still moderately high VOC concentrations after condensation processes, which may require further treatment (e.g. adsorption, or incineration).

Use of equipment at very low temperatures can result in injury to personnel if exposed to the coolant (e.g. liquefied nitrogen) or the recovered product in case of a leak. Many light hydrocarbons form solid hydrates at subambient temperatures which can cause blockage of the condenser and associated pipework. Polymerisation problems may also need to be addressed [113, COM 2006].

Inert gas cycle condensation

Table 3.157: Consumables associated with inert gas cycle condensation

Consumable	Amount	Comments
Nitrogen as inert gas, for emergency purges and/or refrigeration (t/d)	1–2 ([1])	─
Energy (kWh/1 000 Nm^3)	NI	Vents, pumping, cooling facilities
Pressure drop (kPa)	NI	─
([1]) [12, ETBPP 1996]. NB: NI = no information provided.		

Operational data
Design and maintenance [176, Schenk et al. 2009]
For cryogenic condensation, almost any emission level can be achieved, as long as the cooling is strong enough. In practice, it has rarely been lower than -95 °C, with an average temperature between -50 °C and -80 °C. The final dimensioning is based on a careful assessment of the abatement efficiency, the remaining emission and the amount of recovered VOCs on the one hand and the investment and operating costs, including the nitrogen consumption, on the other. Most systems are applied on relatively small gas flows (up to 50 Nm³/h) and for the treatment of batch emissions, for which the system is on standby during most of its operational time. Non-stop systems larger than 250 Nm³/h are less common; the largest units in construction have a range of around 500 Nm³/h. For applications larger than 1 000 Nm³/h condensation temperatures are limited to -30 °C. Systems are usually designed to reach an efficiency of at least 99 %. If necessary, an adsorption technique (e.g. activated carbon and zeolites) is used afterwards in order to meet emission limit values.

Monitoring
The efficiency of the condensation system as an air cleaning system may be determined by monitoring the concentration of the compounds(s) to be abated (e.g. solvent vapours) before and after the condensation system. 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 (the operating conditions of the plant/installation/unit at the time of the grab samples are usually recorded to allow further analysis of the cause of odorous emissions and possibilities for reduction). Ammonia can be chemically determined when wet. A measurement of the dust concentration should take place under isokinetic conditions [176, Schenk et al. 2009]. 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. The condenser has to be defrosted regularly in case ice forms. This can be done by periodically defrosting or by defrosting depending on the amount of ice on the condenser. The system can be fully automated. The pressure drop should be checked in order to prevent leaks [176, Schenk et al. 2009].

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 [12, ETBPP 1996].

Applicability
Coolant condensation
Coolant condensation is applied to relatively 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 an absorbent (provided the substances targeted are soluble in water).

An essential application of coolant condensation is as the 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 3.5.1.2.3), scrubbers (see Section 3.5.1.2.4) and thermal oxidisers (see Section 3.5.1.3.5). On the other hand, condensation is a suitable post-treatment for enriched gas streams, e.g. from membrane separation (see Section 3.5.1.2.1) or waste water stripping (see Section 3.3.2.3.4.17) and distillation (see Section 3.3.2.3.4.14).

Application limits and restrictions are given in Table 3.158.

Table 3.158: Application limits and restrictions associated with coolant condensation

Issue	Limits/restrictions
Gas flow	100–100 000 Nm^3/h
Incoming gas temperature	50–125 °C
Water content	Gas needs to be essentially water-free when condensation is below 0 °C
Pressure	Atmospheric
Pressure drop	Some
Fluid level	Humid or saturated incoming gas stream. The water dew point should be at a temperature of 42 ºC or above
Dust	< 50 mg/Nm^3 (non-sticky)
Odour	> 50 000 ou$_E$/Nm^3. Can only be applied for (odour) compounds easily dissolvable in water
Ammonia	200–1 000 mg/Nm^3
Source: [176, Schenk et al. 2009].	

Cryogenic condensation
Cryogenic condensation can cope with all VOCs and volatile inorganic pollutants, irrespective of their individual vapour pressures. The low temperatures applied allow for very high condensation efficiencies in such a way that it is well-suited as a final VOC emission control technique. On the other hand, temperatures below the freezing point of water require an essentially water-free gas feed. Cryogenic condensation 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 [77, US EPA 2001].

Application limits and restrictions are given in Table 3.159.

Table 3.159: Application limits and restrictions associated with cryogenic condensation

Issue	Limits/restrictions
Gas flow	Up to 5 000 Nm^3/h, standard about < 250 Nm^3/h
Incoming gas temperature	Up to 80 °C
Pressure	2–600 kPa
Pressure drop (mbar)	A few dozen
Fluid level	Dry gas stream; the forming of ice with the condensation may not occur, potentially by dehumidifying
Ingoing pollutant concentration	Up to 1 000 g/Nm^3 for acetone, methyl ethyl ketone, methanol, toluene, VOCs
Source: [176, Schenk et al. 2009].	

Advantages and disadvantages are given in Table 3.160.

Table 3.160: Advantages and disadvantages associated with condensation and cryogenic condensation

Advantages	Disadvantages
Coolant condensation • Compact and robust 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 that is difficult to separate • (Some) 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, the required final concentration can be steered by carefully selecting the condenser temperature • Nitrogen gas is recycled • Good process handling is possible, emissions can at least be calculated approximately	Cryogenic condensation • Not suitable for wet gas streams because of ice formation that impedes heat transfer (in the case of humid gas streams, precautions have to be taken in order to minimise ice forming on the condenser, for example by dehumidifying) • Consumption of liquid nitrogen (needed for nitrogen generation facility), or external delivery of nitrogen instead

Retrofittability information is given in Table 3.161.

Table 3.161: Retrofittability associated with condensation, cryogenic condensation and closed-cycle inert gas condensation

Coolant condensation	Cryogenic condensation	Closed-cycle inert gas condensation
Readily retrofittable when cooling water is available, with the heat exchangers positioned near 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	Difficult to retrofit onto existing production plants; they are better suited to new plants
Source: [12, ETBPP 1996]		

Economics

Economics associated with coolant condensation, cryogenic condensation and closed-cycle inert gas condensation are given in Table 3.162.

Table 3.162: Economics associated with coolant condensation, cryogenic condensation and closed-cycle inert gas condensation

Type of cost ([1])	Costs		
	Coolant condensation	**Cryogenic condensation**	**Closed-cycle inert gas condensation**
Investment costs ([2])	EUR 7500–15 000 ([3])	EUR 400 000 ([3, 4])	NI
Operating costs: Labour	2 hours per week + 1 staff day per year ([5])	1 staff day per week ([5])	NI
Cost-determining parameters	Coolant temperature and flow, airflow and temperature	Gas flow, cooling capacity, targeted emission level	NI
Benefits	Eventual recovery of remaining heat	Recovery of product (in some cases)	NI
([1]) Costs related to the collection and disposal of waste gases are not reflected in this table but can significantly add to the total cost [227, CWW TWG 2009]. ([2]) Per 1 000 Nm³/h. ([3]) [176, Schenk et al. 2009]. ([4]) Excluding secondary techniques and nitrogen storage. ([5]) [11, InfoMil 1999]. NB: NI = no information provided.			

The revenue is the recovered VOCs.

Cost factors are given in Table 3.163.

Table 3.163: Cost factors associated with condensation, cryogenic condensation and closed-cycle inert gas condensation

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)
Source: [12, ETBPP 1996]	

Driving force for implementation
The main driver for using condensation and cryogenic condensation is to pretreat or post-treat waste gases for upstream or downstream waste gas treatment facilities.

Example plants
The technique is reported to be widely used in the chemical industry sector as well as in other sectors such as waste treatments.

Reference literature
[11, InfoMil 1999] [12, ETBPP 1996] [77, US EPA; et al. 2001] [113, COM 2006] [176, Schenk et al. 2009] [227, CWW TWG 2009]

3.5.1.2.3   Adsorption

Description
Adsorption is a heterogeneous reaction in which gas molecules are retained on a solid or liquid surface (adsorbent also referred to as a molecular sieve) that prefers specific compounds to others and thus removes them from effluent streams. When the surface has adsorbed as much as it can, the adsorbed content is desorbed as part of the regeneration of the adsorbent. When desorbed, the contaminants are usually at a higher concentration and can either be recovered or disposed of.

Major types of adsorption systems are:

- fixed-bed adsorption;
- fluidised-bed adsorption;
- continuous moving-bed adsorption;
- pressure swing adsorption (PSA).

Figure 3.62 provides an overview of the different adsorption systems, adsorbents and regeneration processes used.
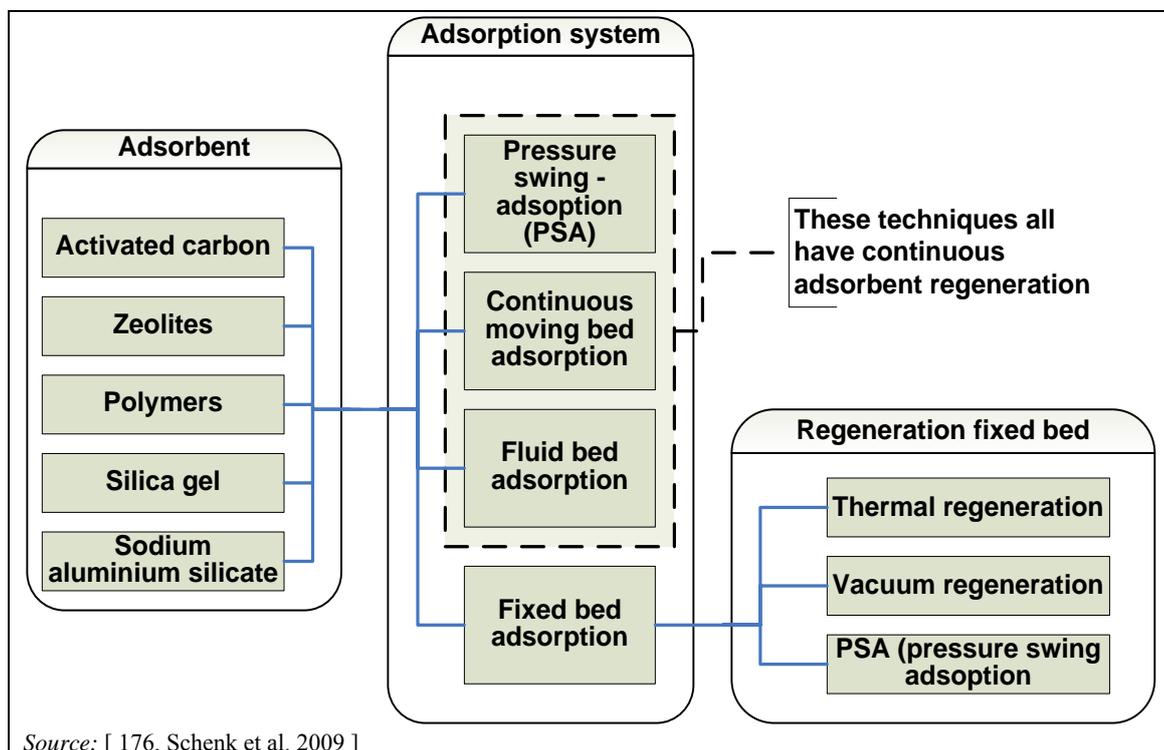
Source: [176, Schenk et al. 2009]

Figure 3.62: Overview of different adsorption systems, adsorbents and regeneration processes used

Fixed-bed adsorption processes (see Figure 3.63) are widely used. If needed, waste gases 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 then fed at about 40 °C to the adsorber, passes upwards and leaves purified. To allow regeneration, adsorbers are normally operated as multiple-bed (two or more) facilities, i.e. one bed is loaded, the other regenerated and, optionally, a third bed is in standby mode. A twin bed adsorption process is illustrated in Figure 3.63.

Figure 3.63: Example of a twin bed adsorption process

Fluidised-bed processes (see Figure 3.64) 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, with the adsorbent regenerated in a heat exchanger underneath the adsorber and subsequently returned pneumatically to the fluidised bed.

Figure 3.64: Fluidised-bed adsorption

With **continuous moving-bed** processes (see Figure 3.65) the adsorbent is continuously fed into the top of the adsorber, passing the gas stream countercurrently. The saturated adsorbent at the bottom of the vessel is continuously transferred to a moving-bed regenerator.
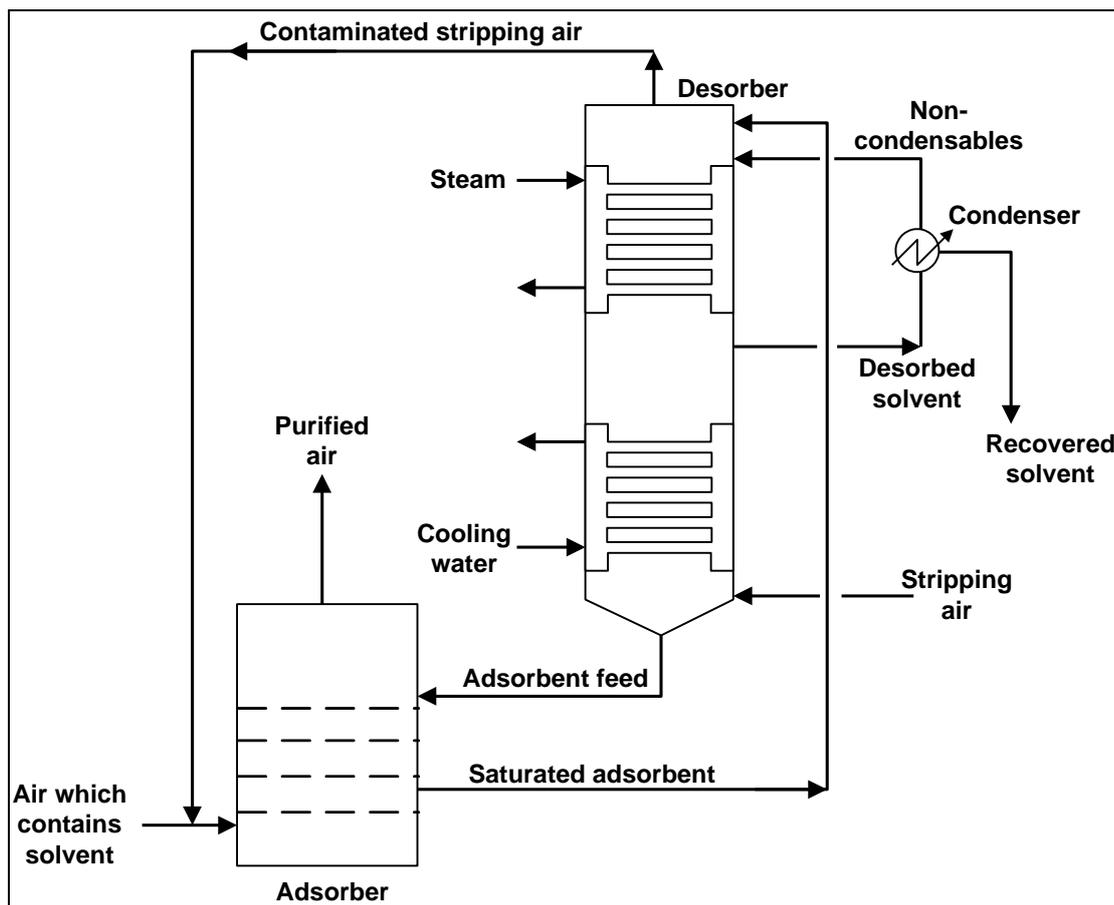
Figure 3.65: Continuous moving-bed adsorption and desorption

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 the production of pure compounds;
Step 3: depressurisation;
Step 4: purging at low pressure or under vacuum.

This four-step process causes a separation of compounds according to the strength with which they bond to the adsorbent. With downstream treatment facilities, this technique improves the ability of waste gas mixtures to be recovered and reused.

Typical adsorbents include [12, ETBPP 1996]:

- **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, e.g. with oxidants such as potassium permanganate or with sulphur compounds (improving the retention of heavy metals) [11, InfoMil 1999];
- **zeolites**, properties depending on their manufacturing, working either as mere molecular sieves, selective ion exchangers or hydrophobic VOC adsorbers;
- macroporous **polymer** particles, which are used as granules or beads, without being highly selective with respect to VOCs;
- silica gel;
- sodium-aluminium silicates.

Polymers can be used in combination with activated carbon and zeolites in an adsorption system. This can be done by using the different adsorbents in series, e.g. with the polymers in the first stage for separating the high VOC concentrations and the zeolites in the second stage for separating the lower VOC concentrations, or it can be done in a mixed bed [176, Schenk et al. 2009].

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.

Thermal-swing regeneration uses several heat sources:

- steam, as the most common,
- microwaves,
- embedded heaters,
- heated inert gas, for safety reasons (to avoid explosive mixture with VOCs).

Superheated steam is passed downward through the adsorbent and thus carries the loaded compounds down to a condensation and separation unit, such as gravitational separators (see Section 3.5.1.4.2) or distillation facilities (see Section 3.3.2.3.4.14). 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, and is suitable to recover and reuse vulnerable substances. This method is applied to GAC, zeolite and polymer adsorbents.

Achieved environmental benefits
Abatement efficiencies and emission levels associated with adsorption are given in Table 3.164.

Table 3.164: Abatement efficiencies and emission levels associated with adsorption

Pollutant	Abatement efficiency (%)	Emission level	Comments
VOCs	80–95 [1]	5–100 mg/Nm^3 [1]	GAC
	99 [1]	NI	Zeolites
	95–98 [1]	10–200 ppm [1]	Polymers
Formaldehyde	NI	< 1 ppm [1]	Polymers
Toluene	90 [1]	NI	GAC
Dioxins/furans	> 98 [1]	< 0.1 ng/Nm^3 TEQ [1]	GAC
Odour	80–95 [1]	NI	GAC
	80–95 [1]	NI	Zeolites
Mercury	> 98 [1, 2]	< 0.05 mg/Nm^3 [1]	GAC
Hydrogen sulphide (H$_2$S)	80–95 [1]	NI	GAC
	> 99 [3]	NI	GAC, < 10 ppmv of H$_2$S in the raw gas
	> 95 [3]	NI	GAC, > 10 ppmv of H$_2$S in the raw gas

[1] Depending on the specific configuration, operational conditions and reagents. Values are based upon half-hourly averages [176, Schenk et al. 2009].
[2] With a fixed-bed filter, removal efficiencies of up to 99.5 % are possible. When cleaning waste gas, powder coal is often used, making efficiencies of up to 98 % possible [176, Schenk et al. 2009].
[3] [167, ADEME 1999].
NB: NI = no information provided.

Cross-media effects
Consumables are given in Table 3.165.

Table 3.165: Consumables associated with adsorption

Consumable	Amount			Comments
	GAC	Zeolites	Polymers	
Steam (desorption) (kg/kg solvent regained)	1.5–6 [1]	[2]	NI	—
Nitrogen gas (hot gas desorption) (Nm^3/t solvent)	35 [1]	NI	NI	—
Cooling water (condensation) (m^3/t solvent)	35–60 [3] 100–150	NI	NI	For all 3 adsorption techniques
Loss of adsorbent (kg/t solvent)	0.5–1 [3]	NI	NI	—
Replacement of adsorbent (m^3 per 10 000 m^3/h of raw gas to treat)	5–15 [4]	NI	NI	To abate H$_2$S
Energy (kWh/t solvent)	35–100 [3] 130–260	NI	NI	—

[1] [12, ETBPP 1996].
[2] Waste water is produced when regenerating zeolite: 4–6 m^3/t regenerated zeolite [176, Schenk et al. 2009].
[3] [9, BASF 1999].
[4] [167, ADEME 1999].
NB: NI = no information provided.

Steam regeneration produces waste water with relatively high loads of contaminants which has to be discharged to waste water treatment. When there is no regeneration (e.g. when using GAC for abating H$_2$S [167, ADEME 1999]), 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.

Small amounts of waste water from the demister are generated when using activated carbon to abate H_2S [167, ADEME 1999].

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 compounds when the adsorbent is hot, resulting in bed fires which also consume part or all of the GAC, but not the 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 is 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. Potential high temperature incidents in carbon beds can also be prevented by monitoring and alarm procedures.

Operational data
Monitoring [19, HMIP 1994]
The abatement efficiency of the system is determined by monitoring the concentration of VOCs/odour before and after the adsorption system. VOCs can be measured as total carbon (excluding particulate matter), using a flame ionisation detector (FID). 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 abatement efficiencies for sulphur compounds are determined using gas chromatography with flame photometric detection (GC-FPD) analysis.

The most important measurement is the pressure drop across the dust filters (if fitted) 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 some new systems based on breakthrough sequencing of the beds: when the emission level from an operating bed reaches a preset 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 [12, ETBPP 1996].

The adsorption process typically has a number of valves, which automatically open and close in sequence, generally on a time basis (of every 12 to 15 minutes). The units, therefore, require daily inspection to ensure continued efficient operation, and routine maintenance [113, COM 2006].

Applicability

The application of adsorption encompasses:

- the recovery of VOCs (raw material, product, solvent, etc.) for reuse or recirculation; it may be used as a stand-alone system, as a concentration step to improve the viability of further recovery operations such as membrane separation (see Section 3.5.1.2.1) or to treat the tail gas emissions from an abatement system;
- the abatement of pollutants (hazardous substances from production or treatment facilities (e.g. WWTP) such as VOCs, H_2S, odours, trace gases, etc.) that cannot be recirculated or otherwise used, possibly with GAC as an adsorbent, not regenerated but incinerated;
- the use as a guard filter after final treatment facilities.

The possibilities for VOC recovery may be restricted by the presence of H_2S. In that case, an additional GAC bed could be installed at the inlet which would need to be replaced periodically as it cannot be regenerated [228, CWW TWG 2011].

The application of adsorption as an abatement technology without recovery 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) VOCs and organic hazardous air pollutant emissions, e.g. emissions from:

- degreasing;
- paint spraying;
- solvent extraction;
- metal foil coating;
- plastic film coating;
- paper coating;
- pharmaceuticals.

Application limits and restrictions are given in Table 3.166.

Table 3.166: Application limits and restrictions associated with adsorption

Issue	Limits/restrictions		
	GAC	**Zeolites**	**Polymers**
Gas flow (Nm^3/h)	100–100 000 ([1])	< 100 000 ([1])	NI
Temperature (°C)	15–80 ([1]), Ideally about 20 ([2])	< 250 ([1])	Low ([2])
Pressure (MPa)	0.1–2 ([1])	Atmospheric ([1])	NI
Pressure drop (mbar)	10 to 50 ([2, 3, 4])	NI	NI
VOC content (mg/Nm^3)	Maximum 25 % of LEL 10–50 000 ([2])	Maximum 25 % LEL	Maximum 25 % LEL 500–2 000 ppm ([2])
Dioxins content (ng/Nm^3 TEQ)	10–100 ([1])	NI	NI
Odour content (ou_E/m^3)	5 000–100 000 ([2])	NI	NI
Mercury content (mg/Nm^3)	1–10 ([2])	NI	NI
H_2S content (ppm)	Maximum of 1 000	NI	NI
Dust content (mg/Nm^3) (PM size not identified)	Low concentration to prevent obstruction ([2])	Low concentration to prevent obstruction ([2])	Low concentration to prevent obstruction ([2])
Relative humidity of the waste gas	Maximum of 70 % ([5])	NI	Less critical than with GAC ([2])
([1]) [11, InfoMil 1999]. ([2]) [176, Schenk et al. 2009]. ([3]) [9, BASF 1999]. ([4]) [228, CWW TWG 2011]. ([5]) At humidity levels above 70 %, the efficiency will decrease because of the water taking up the active spaces in the activated carbon [176, Schenk et al. 2009]. NB: NI = no information provided.			

Advantages and disadvantages are given in Table 3.167.

Table 3.167: Advantages and disadvantages associated with adsorption

Advantages	Disadvantages
General • High efficiency for VOC removal and recovery • Simple and robust technology • High saturation level of the adsorbent • Simple installation • Relatively simple maintenance • Suitable for discontinuous processes	General • Particulates in the waste gas stream can cause problems (i.e. clogging) • Mixtures can cause a fast bleeding of the bed
GAC • Wide efficiency range • Not restricted to polar or non-polar compounds	GAC • Usually not suitable for very high VOC concentrations (i.e. for VOC concentrations > 50 mg/Nm^3) • Not suitable for wet gases (not as critical with impregnated activated carbon) • Risk of bed fires • Potential for polymerisation of unsaturated organic compounds on GAC
Zeolites • Very suitable for low VOC concentrations • Not as sensitive to fluids/humidity as GAC [69, US EPA 1999]	Zeolites • Restrictions concerning adsorption area compared to other adsorption techniques [69, US EPA 1999] • Not suitable for wet waste gas streams • Risk of bed fires
Polymers • Easy desorption of the VOCs • No tendency towards catalytic reactions that cause self-ignition • Long lifespan • Not as sensitive to fluids/humidity as GAC • Suitable for discontinuous processes	Polymers • High initial costs

Economics

Economics associated with adsorption are given in Table 3.168.

Table 3.168: Economics associated with adsorption

Type of cost	GAC	Zeolites (^{1})	Polymers	Comments
Investment costs (per 1 000 Nm^3/h)	EUR 10 000–50 000	Very variable, depending on application and design	NI	—
Operating costs:	Low, except for the purchase of activated carbon	1 000–3 000 EUR/t VOC	NI	—
Labour	A few days per year, depending on the specific design			
Energy	Low	NI	NI	—
Consumables (EUR/kg of adsorbent replaced)	0.8–6	20–100	20–100	Including disposal. Polymers are about twenty times as expensive as GAC.
Cost-determining parameters	Concentration of pollutant, flow of gas stream, lifespan of the filter	Gas flow, filtering material, fabric load, odour load	NI	—
Benefits	Potential material recovery in the regeneration stage	No material recovery possible	No material recovery possible	—

(^{1}) Costs for zeolites concern hydrophobic zeolite.
NB: NI = no information provided.
Source: [176, Schenk et al. 2009].

Cost factors are given in Table 3.169.

Table 3.169: Cost factors associated with adsorption

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 loading	Use of utilities (steam or electricity) in adsorption/desorption cycle and rate of adsorbent degradation
Presence of impurities	Reducing lifetime of adsorbent
Ease of solvent desorption	Desorption temperature

Source: [12, ETBPP 1996]

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 [12, ETBPP 1996].

Driving force for implementation
Adsorption technology is used for abating, as well as to recover, recycle or prepare (for downstream treatment), inorganic compounds, VOCs and other organic hazardous air pollutant emissions.

Example plants
The technique is reported to be widely used in the chemical industry sector as well as in other sectors such as surface treatment using solvents, foundries, iron and steel production, the food industry, waste incineration, and waste treatments.

Reference literature
[9, BASF 1999] [11, InfoMil 1999] [12, ETBPP 1996] [19, HMIP 1994] [69, US EPA 1999] [104, COM 2003] [113, COM 2006] [167, ADEME 1999] [176, Schenk et al. 2009] [228, CWW TWG 2011] [250, Ullmann's 2011]

3.5.1.2.4 Wet gas scrubber

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 chemical recovery, whereas chemical scrubbing is restricted to removing and abating gaseous compounds. Physico-chemical scrubbing takes an intermediate position. The compound is dissolved in the absorbing liquid and involved in a reversible chemical reaction, which enables the recovery of the gaseous compound [250, Ullmann's 2011].

The major waste gas treatment applications of scrubbing processes are:

- the removal of gaseous pollutants, such as hydrogen halides, SO_2, ammonia, hydrogen sulphide (H_2S) or volatile organic solvents (see also Table 3.147);
- the removal of dust with certain types of scrubbers (see Section 3.5.1.4.5).

Depending on the pollutants to be removed, several aqueous scrubbing liquids are used including the following:

- Water, to remove solvents and gases such as hydrogen halides or ammonia, with the main aim being to recover and reuse these contaminants.
- Alkaline solutions (e.g. caustic soda – i.e. sodium hydroxide – and sodium carbonate), to remove acidic compounds such as hydrogen halides, sulphur dioxide, hydrogen sulphide (H_2S), phenols, chlorine; also used for second-stage scrubbing to remove residual hydrogen halides after first-stage aqueous absorption; biogas desulphurisation. The pH value of the alkaline scrubber depends on the pollutant to be removed; pH is often kept between 8.5 and 9.5 (for SO_2 removal a pH range of 6.5–7.5 is needed, whereas for H_2S removal a pH of 10 or more is required). The pH value should not be too high because of absorption of CO_2 in the water. A pH value of 10 and above will cause the dissolved CO_2 to be present in the water as carbonate, causing the alkaline consumption rate to increase dramatically. The calcium carbonate will also deposit on the gaskets, increasing the pressure drop. To avoid this, softened water can be used in an alkaline gas scrubber [176, Schenk et al. 2009].
- Alkaline oxidative solutions, i.e. alkaline solutions with oxidants such as sodium hypochlorite (NaOCl), chlorine dioxide (ClO_2), ozone (O_3) or hydrogen peroxide (H_2O_2) – see Section 3.5.5.4.2.2 for an application to treat odorous pollutants.
- Oxidising solutions – see Section 3.5.1.5.5 for an application to recover NO_X from concentrated waste gases.
- Sodium hydrogen sulphite solutions, to remove odour (e.g. aldehydes).
- Na_2S_4 solutions to remove mercury from waste gas.

- Acidic solutions, to remove alkaline compounds, e.g. ammonia, amines and esters. The dosing of the acid is done by means of pH regulation. In most cases, the pH is kept between 3 and 6. Sulphuric acid (H_2SO_4) is often the acid of choice for economic reasons. For specific applications, for example the removal of NH_3, nitric acid (HNO_3) is used [176, Schenk et al. 2009].
- Monoethanolamine and diethanolamine solutions, suitable for the absorption and recovery of hydrogen sulphide.
- Organic solvents with low volatility, e.g. chilled nonane for the recovery of light VOCs such as butanes and pentanes.

Various types of scrubbers are operated, such as:

- fibrous packing scrubbers;
- moving-bed scrubbers;
- packed-bed scrubbers;
- impingement plate scrubbers;
- spray towers.

Their choice depends on the following:

- requirements for performance efficiency,
- energy needs,
- reagents,
- properties of the waste gas stream.

An optimum design of scrubbing systems to achieve low exit concentrations includes high reliability, automatic operation and a countercurrent flow of liquid and gas. Scrubbers are commonly operated with precoolers (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 a gas inlet and outlet, which contains 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 compounds (hydrogen fluoride, hydrogen chloride, sulphuric acid and chromic acid) and organic/inorganic compounds from effluent gas streams.

The blockage of nozzles, the plugging of fibre beds and the 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 prefilter is generally used to remove larger particles from the gas stream prior to its entering the scrubber [45, US EPA 2003].

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 scales might be formed. A typical device is shown in Figure 3.66.

Source: [19, HMIP 1994]
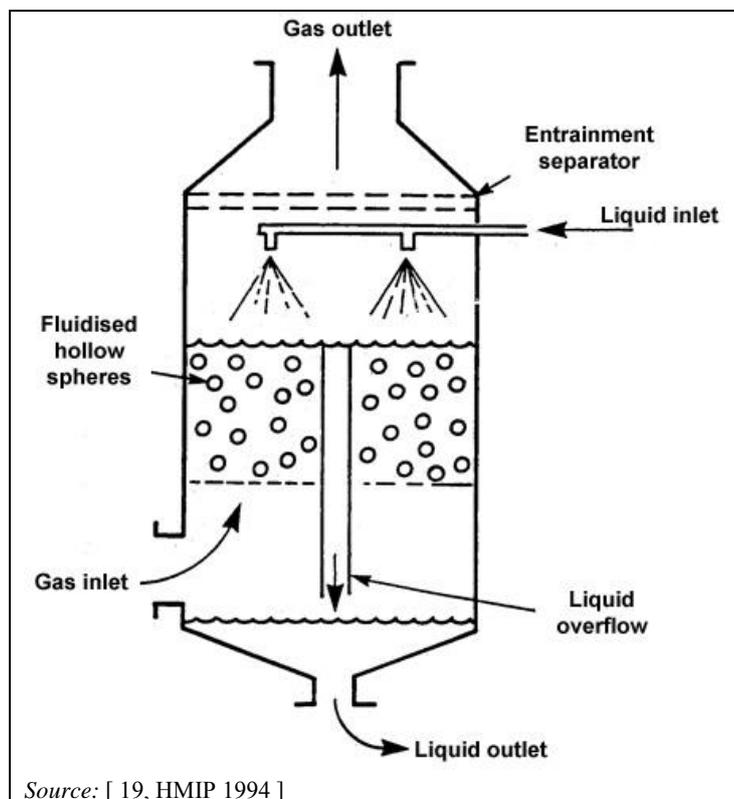
Figure 3.66: Moving-bed scrubber

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-shaped mobile packing resists clogging. This constant movement and the smooth surface of the balls prevent scales 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 (countercurrent 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 VOCs. A typical example is shown in Figure 3.67.

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 in other scrubber designs. Consequently a separate, very efficient, particulate abatement device may be necessary before a packed-bed absorber.

Source: [19, HMIP 1994]
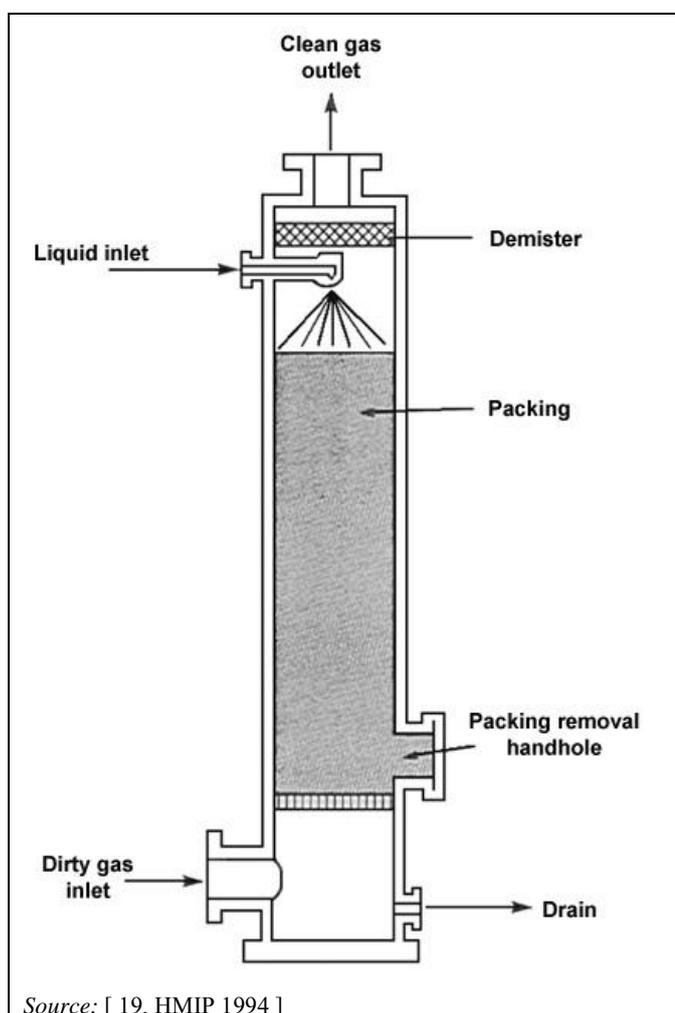
Figure 3.67: Packed-bed scrubber

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 3.68.

Plate scrubbers are not suitable for foaming liquids. When absorption is used to abate VOCs, 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 a cost-efficiency basis. At high gas flow rates, plate towers exhibit larger pressure drops and have larger liquid hold-ups.

Source: [19, HMIP 1994]
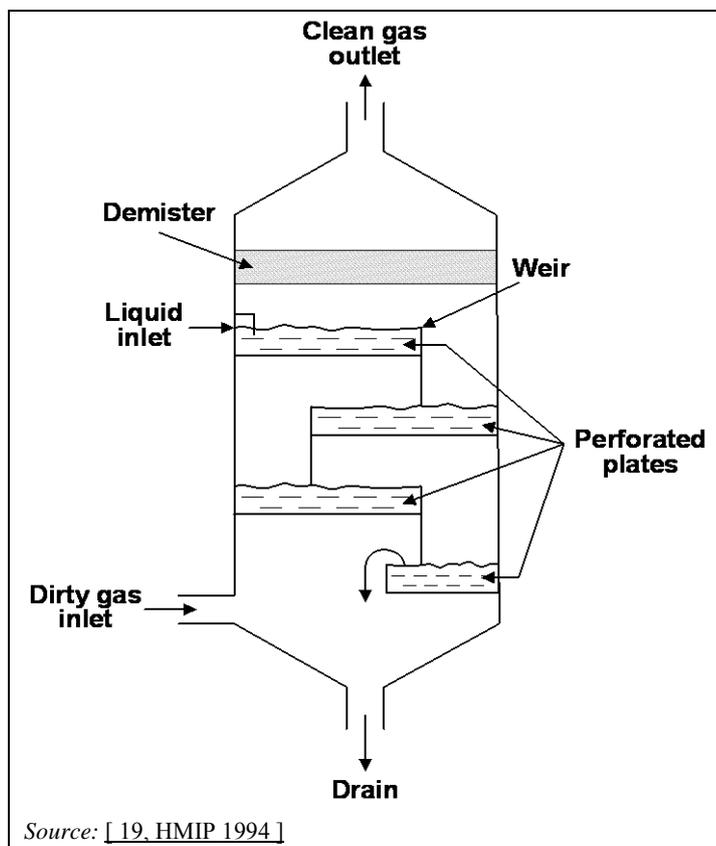
Figure 3.68: Impingement or plate scrubber

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 corrosion-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 countercurrent to the liquid flow. The typical application for spray towers is to remove acid gases and odours. An example is shown in Figure 3.69.
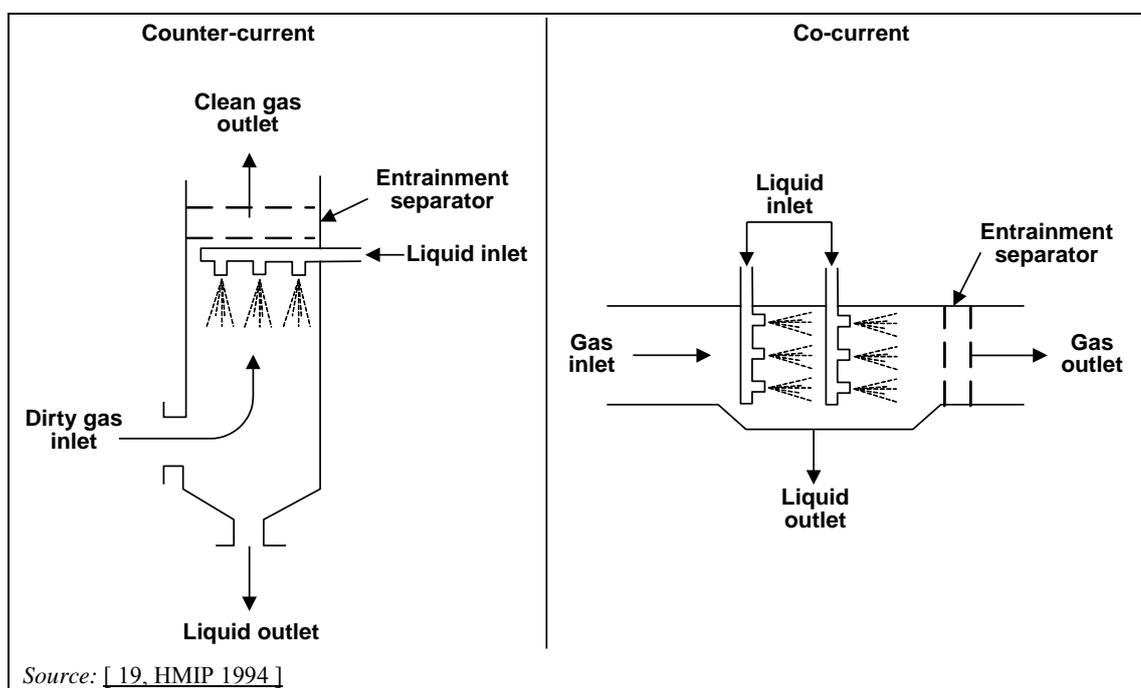
Figure 3.69: Spray tower

The 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 (see Section 3.5.1.5.2). 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 mg/Nm^3 to 10 000 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 regeneration of the adsorbed organic content is distillation (see Section 3.3.2.3.4.14) or steam stripping (see Section 3.3.2.3.4.17), 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 reused directly in the process or segregated into its components, e.g. by distillation. Stripping and distillation are carried out at a reduced pressure in order to reduce the temperature and minimise the degradation risk of the organic compounds [12, ETBPP 1996].

A typical absorption/desorption system is shown in Figure 3.70. The vacuum desorption, as described in Figure 3.70, is not generally applied, but is an option. It makes it easier to boil the scrubbing liquid (solvent), but makes its condensation more difficult.
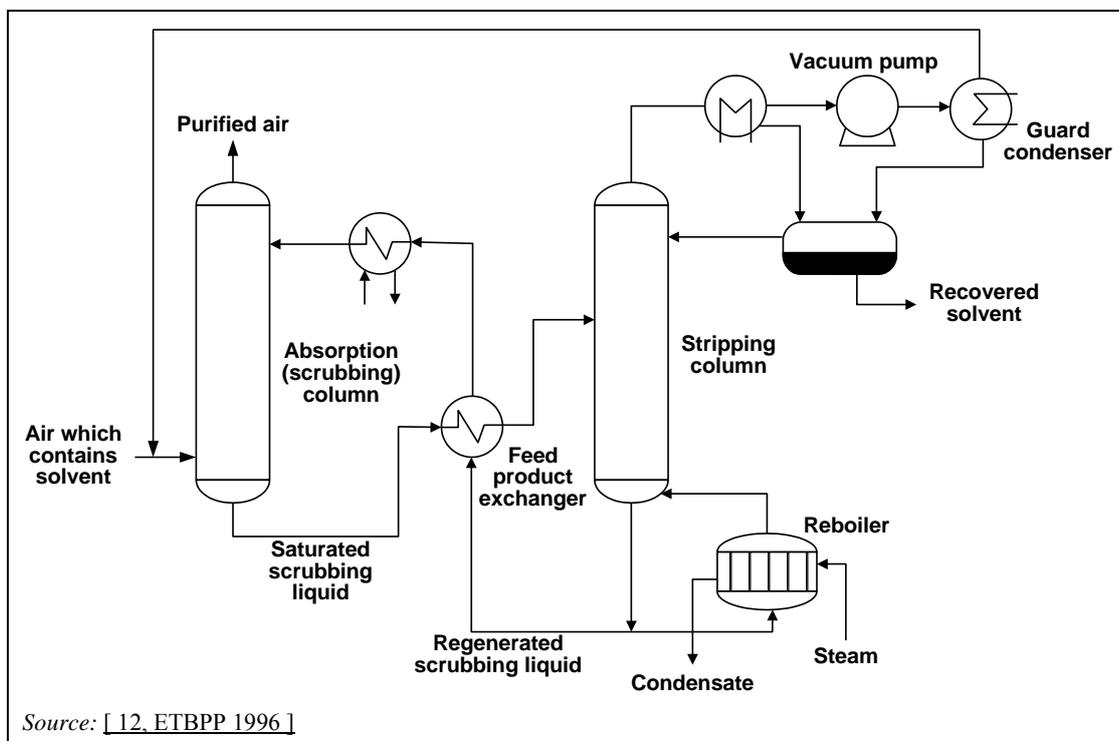
Figure 3.70: Typical absorption/desorption system

Achieved environmental benefits
The abatement efficiency of gas scrubbers is dependent on the residence time of the gas in the absorption section, the type of packing used, the liquid to gas ratio (L/G), the refreshing rate, the temperature of the water and the addition of chemicals. Gravity and centrifugal force play a more important role in the removal of particles with dust scrubbers than with gas scrubbers (see Section 3.5.1.4.5). The addition of chemicals is more typical of gas scrubbers [176, Schenk et al. 2009].

Abatement efficiencies and emission levels associated with wet scrubbers for gas removal are given in Table 3.170.

Table 3.170: Abatement efficiencies and emission levels associated with wet scrubbers for gas removal

Pollutant	Abatement efficiency ([1]) (%)	Emission level (mg/Nm³))([2])	Washing liquid
Alcohols	30–99 ([3])	> 100 ([3])	Water
Hydrogen fluoride	> 99 ([3, 4])	< 50 ([3, 5])	Water
	99 ([3])	< 1 ([3, 5])	Alkaline
Hydrogen chloride	99 ([3, 4])	< 10 ([3])	Water
	99 ([3])	< 10 ([3, 5])	Alkaline
Chromic acid	99 ([3])	< 10 ([3])	Water
Odour	20–45 ([6])	NI	Water
	60–85 ([3])	NI	Alkaline and water scrubbing
Ammonia	> 99 ([3])	< 1 ([5, 7])	Acid and water
Amines	> 99 ([4, 7])	< 1 ([5, 7])	Acid and water
Esters	80 ([3])	NI	Acid
Ethylene oxide	99 ([3])	NI	Acid
Sulphur dioxide	95–98 ([3])	< 10 ([3, 7])	Water
	> 85 ([8])–99 ([3, 9])	< 10 ([3, 9])	Alkaline
	NI	70–75 mg/Nm³ ([10])	NI
Phenols	90 ([3])	NI	Alkaline
Hydrogen sulphide	90–95 ([4, 7])	< 10 ppm ([3])	Alkaline
	80–> 99 ([4, 11, 12])	NI	NI
Inorganic compounds	95–99 ([4, 11, 12, 13, 14, 15, 16])	NI	NI
VOCs	99 ([3])	NI	NI
	50–95 ([4, 13, 15, 17])	NI	NI
	70–> 99 ([4, 14, 16, 18, 19])	NI	NI

([1]) Efficiency depends on the specific plant configuration, operational conditions and reagents used; unless indicated otherwise, performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given have to be used with extreme caution for permitting [176, Schenk et al. 2009].
([3]) [176, Schenk et al. 2009].
([4]) High feed concentration.
([5]) Low feed concentration.
([6]) [227, CWW TWG 2009].
([7]) [11, InfoMil 1999].
([8]) [185, UBA DE 2009]
([9]) The SO₂ abatement efficiency of 99 % and emission level of < 10 mg/Nm³ are pilot-scale performances of the wet scrubber. It was reported in October 2010 that a full-scale installation of the wet scrubber is under construction [177, van Berkel 2010].
([10]) Information provided by CEFIC [227, CWW TWG 2009].
([11]) Impingement plate scrubber.
([12]) [46, US EPA 2003].
([13]) Spray tower, several reagents.
([14]) Packed-bed scrubber.
([15]) [49, US EPA 2003].
([16]) [48, US EPA 2003].
([17]) May achieve > 99 %.
([18]) Fibrous packing scrubber.
([19]) [45, US EPA 2003].
NB: NI = no information provided.

Cross-media effects
The main utilities and consumables required for absorption systems are given in Table 3.171 [12, ETBPP 1996].

The consumption of scrubbing water depends to a great extent on the incoming and outgoing concentrations of gaseous compounds. Evaporation losses are primarily determined by the temperature and the humidity of the incoming gas stream. The outgoing gas stream is, in most cases, completely saturated with water vapour [176, Schenk et al. 2009].

Table 3.171: Consumables associated with wet scrubbers for gas removal

Consumable	Amount	Comments
Scrubbing water	Strongly depends on the application ([1])	–
Chemicals (acids, alkali, oxidants)	NI	–
Desorption facilities: cooling water for condenser, steam for steam stripper	30–40 kg/1 000 Nm^3 waste gas (steam 120 °C) ([2])	–
Energy (kWh/1 000 Nm^3)	0.2–0.5 ([1]) (general) 0.2–1 (acid scrubber) ([1]) 0.02–0.1 (alkaline scrubber) ([1])	Dependent on application, desorption not included
Pressure drop (kPa)	0.4–0.8 ([1])	Dependent on application
([1]) [176, Schenk et al. 2009]. ([2]) [12, ETBPP 1996]. NB: NI = no information provide.		

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 otherwise used (in some cases it can be evaporated and processed for the recovery of products). In Germany, a waste incineration plant for liquid waste and waste gases recycles the scrubbing liquid back into the system and evaporates it in the combustion chamber which results in a waste water-free plant. Moreover, the energy generated in the waste incineration plant is used for the production of steam [191, UBA DE 2009].

Acid scrubbing water is partially drained in order to control the pH. The drained scrubbing water has to be treated before it is discharged [176, Schenk et al. 2009]. Alkaline scrubbing water is also partially drained, to regulate the pH or to prevent the deposition of salts. The drained water, in most cases, requires treatment before being discharged. In some cases, the water can be reused, for example in the production of plaster in the case of SO_2 removal [176, Schenk et al. 2009]. Adequate treatment is desorption of the waste gas content, which is carried out in any case when recovery of the gas is the aim of scrubbing. Desorption can cause emissions to air. Energy needs should be kept in mind.

Operational data
Design and maintenance [176, Schenk et al. 2009]
An optimally designed scrubbing system with low emissions requires a high level of reliability, full automation and a good level of maintenance. The most important design parameters are gas flow, operational temperature, maximum temperature and waste gas composition. When designing an acid or alkaline scrubbing system, synthetic material is used as the primary construction material.

Monitoring [19, HMIP 1994]
The abatement efficiency of the scrubbing system is determined by monitoring the gaseous pollutant concentration before and after the scrubbing system. Sulphur dioxide is usually monitored with infrared analysers; wet chemical methods are used for hydrogen halides. VOCs 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 reduction potential.

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 be detected quickly, and adequate instrumentation with alarms 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 reduction potential 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 are 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 [12, ETBPP 1996].

Applicability
Scrubbing or absorption is widely used as a raw material and/or product recovery technique for the separation and purification of gaseous streams which contain high concentrations of VOCs, 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 VOCs. Its suitability as a pollution control method depends on:

- the 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 a suitable solvent/chemical reagent.

Absorption is enhanced by:

- larger contacting surfaces;
- higher liquid/gas ratios;
- higher concentrations in the gas stream;
- lower temperatures.

Low outlet gas concentrations will typically be required for hazardous VOCs, leading to impractically tall absorption towers, long contact times and high liquid to gas ratios that may not be cost-effective. Therefore, wet scrubbers are more effective for hazardous VOC control when used in combination with other control devices, such as GAC adsorbers (see Section 3.5.1.2.3) or waste gas oxidisers (see Sections 3.5.1.3.5 and 3.5.1.3.6).

Application limits and restrictions are given in Table 3.172.

Table 3.172: Application limits and restrictions associated with wet scrubbers for gas removal

Issue	Limits/restrictions
Gas flow (Nm³/h)	50–500 000 [1]
	1 800–170 000 (fibrous packing scrubber) [2]
	900–130 000 (packed-bed scrubber) [3]
	1 700–130 000 (impingement plate scrubber) [4]
	2 500–170 000 (spray tower) [5]
Temperature (°C)	5–80 (general) [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 oxidative scrubbing) [1]
	30 (biogas desulphurisation) [1]
	(high gas temperatures can lead to significant scrubbing liquid evaporation losses)
Pressure	Atmospheric
Pressure drop (mbar)	4–8 (acid scrubbing) [6]
Pollutant loading (g/Nm³)	0.2–11 (fibrous packing scrubber) [2]
Particulates content (mg/Nm³)	< 10; for a good performance low dust concentrations are required. Scrubbers that are designed for removing dust can work with higher dust concentrations (see Section 3.5.1.4.5) [6]
Alcohols content (mg/Nm³)	200–5 000 [6, 7]
Ammonia content (mg/Nm³)	200–1 000 (acid scrubbing) [6]
Amines content (mg/Nm³)	10–1 000 (acid scrubbing) [6]
Esters content (mg/Nm³)	> 100 (acid scrubbing) [6]
HCl content (mg/Nm³)	50–20 000 [6, 8]
HF content (mg/Nm³)	50–1 000 [6]
Phenols content (mg/Nm³)	< 5 000 [6]
SO₂ content (mg/Nm³)	100–10 000 [6]
H₂S content (mg/Nm³)	1 000–10 000 ppm [6]
[1] [11, InfoMil 1999]. [2] [45, US EPA 2003]. [3] [48, US EPA 2003]. [4] [46, US EPA 2003]. [5] [49, US EPA 2003]. [6] [176, Schenk et al. 2009]. [7] With water scrubbing. [8] With alkaline scrubbing.	

Advantages and disadvantages are given in Table 3.173.

Table 3.173: Advantages and disadvantages associated with wet scrubbers for gas removal

Advantages	Disadvantages
General • Wide range of uses • Very high abatement efficiency can be achieved • Compact installation thanks to a favourable ratio between capacity and device volume • Simple and robust technology • Simple maintenance • Only few wear-sensitive components • Can handle flammable and explosive gases/dusts with little risk • Can also cool hot gas streams (quencher) • Can handle mists • Corrosive gases and dusts can be neutralised • Can be constructed in modules	General • Water or diluted chemicals are required for the 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 reuse or for disposal operations • For roof fitting, support structures are needed • Sensitive to corrosion. For outdoor fitting, frost protection is needed (depending on climate) • Packing material sensitive to clogging because of dust or grease • Collected particulates may be contaminated and may not be recyclable • Off-gas may require reheating to avoid visible (steam) plume • For treating odour problems, pilot-scale tests are required in order to evaluate the abatement potential of the system • Recirculation of scrubbing liquid may cause an increase in odour emission
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 investment costs • 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
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 compared to other wet scrubbers • Low investment costs compared to other wet scrubbers • Relatively free of plugging • Relatively small space requirements • Capable of collecting 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 operating costs

Retrofitting to existing plants can be difficult because of limited space availability and/or complicated modifications to existing flue-gas piping systems, which could require a long plant shutdown for implementation of the scrubbing system. Retrofits of existing absorption systems with improved structured packing and/or liquids can also be carried out to improve the operation of recovery equipment [12, ETBPP 1996] [227, CWW TWG 2009].

Economics
Economics associated with wet scrubbers for gas removal are given in Table 3.174.

Table 3.174: Economics associated with wet scrubbers for gas removal (without waste water treatment)

Type of costs	Costs				
	Fibrous packing	**Moving bed**	**Packed-bed**	**Impingement plate**	**Spray towers**
Investment costs (per 1 000 Nm³/h)	USD 600–1 800 (EUR 460–1 380) ([1])	NI	USD 6 300–32 500 (EUR 6 730–34 700) ([2])	USD 1 300–7 000 (EUR 1 390–7 480) ([3])	USD 500–2 200 (EUR 540–2 350) ([4])
	General: EUR 2 500–25 000 depending on the design ([5]) Acid scrubber: EUR 7 500–25 000 depending on the scale and design ([5]) Alkaline scrubber: EUR 2 500–35 000 depending on the scale and design ([5])				
Annual operating costs (per 1 000 Nm³/h)	USD 1 000–21 100 (EUR 770–16 100) ([1])	NI	USD 9 300–28 900 (EUR 9 940–30 900) ([2])	USD 1 500–42 000 (EUR 1 600–44 900) ([3])	USD 800–28 100 (EUR 850–30 000) ([4])
Operating costs: Time Labour Consumables	About 4 h/week ([5]) EUR 5 000–8 000/yr ([5]) About EUR 150/t (for acids); about EUR 200/t (for caustic soda) ([5])				
Cost-effectiveness (per tonne per year of pollutant abated)	USD 40–710 (EUR 31–540) ([1])	NI	USD 110–550 (EUR 120–590) ([2])	USD 51–1 300 (EUR 54–1 390) ([3])	USD 28–940 (EUR 30–1 000) ([4])
Cost-determining parameters	Gas flow, reagents and eventual remaining emission treatment (waste water)				
Benefits	Potential recovery of products for water and acid scrubbers; commonly none for alkaline scrubbers				

([1]) Cost data for 1995 [45, US EPA 2003]. Average currency conversion rate for 1995: EUR/USD = 1.307.
([2]) Cost data for 2002 [48, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([3]) Cost data for 2002 [46, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([4]) Cost data for 2002 [49, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([5]) [176, Schenk et al. 2009].

Cost factors are given in Table 3.175.

Table 3.175: Cost factors associated with wet scrubbers for gas removal

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
Source: [12, ETBPP 1996]	

Driving force for implementation
Drivers for using scrubbing are:

- raw material and/or product recovery in gaseous streams containing high concentrations of VOCs, especially compounds soluble in water such as alcohols, acetone or formaldehyde;
- abatement of inorganic compounds.

Example plants
Wet gas scrubbing is reported to be widely used in the chemical industry sector as well as in other sectors such as surface treatment, storage and handling of chemicals, and waste incineration.

Acidic scrubbing is commonly used in the chemical industry sector as well as in other sectors such as manure processing, composting, waste processing (ammonia, amines), foundries (amines), and the production of fish feed (amines).

Alkaline scrubbing is commonly used in the chemical industry sector as well as in other sectors such as storage and handling of chemicals, waste incineration (e.g. at a chemical site in Germany [185, UBA DE 2009]), sludge-processing installations, sewerage water pumping stations, and waste water treatment plants.

Example plants include central waste gas treatment and waste incineration plants in Germany [185, UBA DE 2009] [186, UBA DE 2009] [187, UBA DE 2009] [191, UBA DE 2009].

Reference literature
[11, InfoMil 1999] [12, ETBPP 1996] [19, HMIP 1994] [45, US EPA 2003] [46, US EPA 2003] [48, US EPA 2003] [49, US EPA 2003] [176, Schenk et al. 2009] [177, van Berkel 2010] [185, UBA DE 2009] [186, UBA DE 2009] [187, UBA DE 2009] [191, UBA DE 2009] [227, CWW TWG 2009] [250, Ullmann's 2011]

3.5.1.3 Abatement techniques for VOCs and inorganic compounds

3.5.1.3.1 Biofiltration

Description

The waste gas stream is passed through a bed of organic material (such as peat, heather, compost, root wood, tree bark, peat, compost, softwood and different kinds of combinations) or some inert material (such as clay, activated carbon, and polyurethane), where it is biologically oxidised by naturally occurring microorganisms into carbon dioxide, water, inorganic salts and biomass.

A biofilter construction is shown in Figure 3.71.

Source: [19, HMIP 1994]
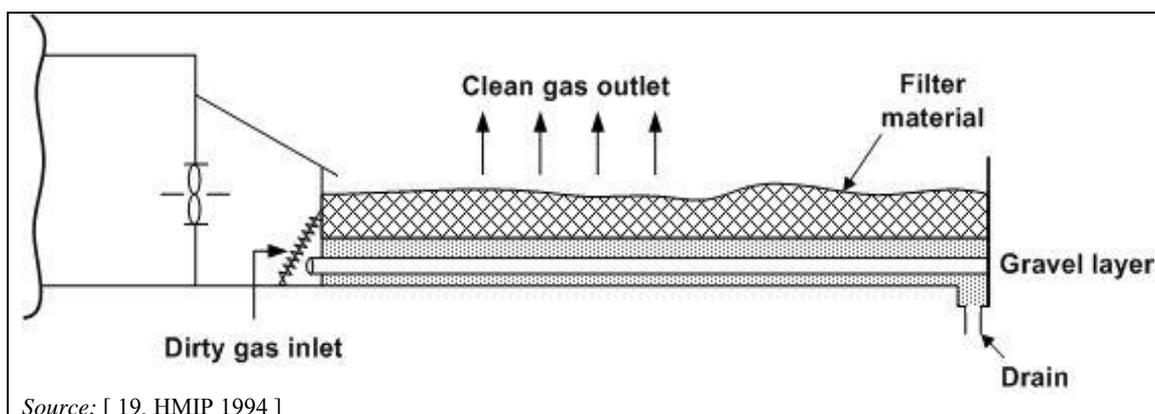
Figure 3.71: Biofilter construction

Biofilters can be divided into:

- open biofilters;
- enclosed biofilters.

An open biofilter consists of a layer of porous biofiltering material underlaid 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 to this is the use of multi-level biofilters, where several layers set above one another obviate the need for a large area. In areas with a 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 biofilters in operation are open-bed filters, which are less costly than enclosed biofilters but also 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 microorganisms are enclosed in a fixed bed. The height of the filter material is between 0.5 m 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. In France, best practices show that the height of the filter material should be at least 1 m to obtain a residence time between 15 s and 60 s and the specific load is between 100 and 150 Nm^3/h per m^2 [227, CWW TWG 2009].

Parameters such as biofilter media pH, moisture content (relative gas moisture of about 95 % and more is required) and inlet gas temperatures affect odour removal capacity.

The moisture balance is regulated by a preconnected humidifier or gas scrubber, at times in combination with a moistening of 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 are substantially below 0 °C.

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 a 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, e.g. of odour, depends on the pollutant concentration. As a rough guide, a minimum residence time of 30 s to 45 s should be aimed for.

The material quality and the process operation of biofilter machinery need to offer protection against corrosion. The removal of condensed water from ducts needs to be ensured [4, Braun et al. 1994].

A typical biofilter process is shown in Figure 3.72. It includes a wet scrubber as a pretreatment facility.


Source: [9, BASF 1999]
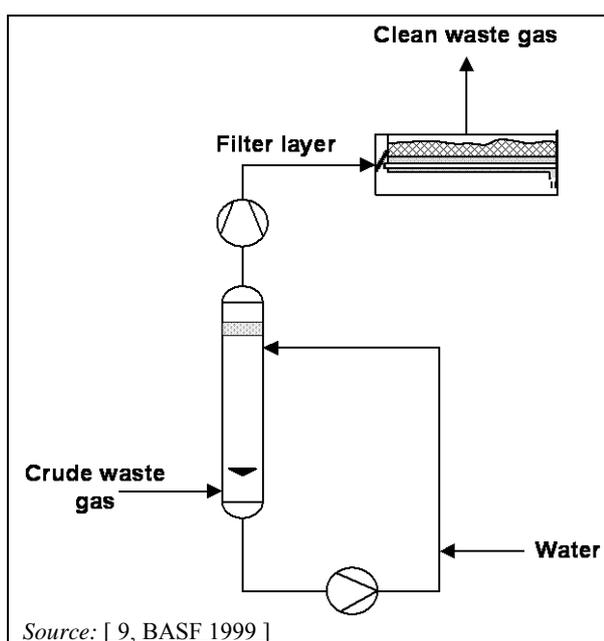
Figure 3.72: Typical biofilter process

Achieved environmental benefits
Abatement efficiencies and emission levels associated with biofiltration are given in Table 3.176.

Table 3.176: Abatement efficiencies and emission levels associated with biofiltration

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm^3)	Comments
VOCs	75–95 ([3])	5–50 ([4])	—
Toluene	80–95 ([3])	5–20 ([4])	—
Styrene	80–90 ([3])	10–50 ([4])	—
Carboxylic acid esters	77–89 ([5])	10 ([5])	At a German plant with a waste gas volume of 30 000 Nm^3/h
Ethanol	> 90 ([6])	NI	—
Odour	70 ([2])–99 ([7])	< 1 000 ou$_E$/Nm^3 ([3])	—

([1]) Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].
([3]) [176, Schenk et al. 2009].
([4]) [182, Martin 2010].
([5]) Concentration reported is the daily average value averaged across the filter area (volumetric flow-weighted average) [180, UBA DE 2009].
([6]) [200, Wang et al. 1996].
([7]) [104, COM 2003]: indicative application range 10 000–200 000 ou$_E$/Nm^3.
NB: NI = no information provided.

For some odorous compounds (e.g. mercaptans, H$_2$S), abatement efficiencies of 75 % are a minimum. Using a scrubber and biofilter in combination can increase performance. For other odorous compounds, the abatement efficiency is somewhat lower. Comparative research for odour abatement efficiencies between scrubbers (see Section 3.5.1.2.4) and biofilters show that biofilters achieve higher efficiencies [176, Schenk et al. 2009].

Cross-media effects
Percolate water from the biofilter is polluted with decomposition products (e.g. nitrate, sulphate) and organic materials. This waste water needs to be treated. Periodically, the filter bed material should be replaced and disposed of (e.g. composted or incinerated) [176, Schenk et al. 2009].

When no waste gas is being treated, fresh air has to be injected through the biofilter to keep the microorganisms alive [180, UBA DE 2009].

The consumables are given in Table 3.177.

Table 3.177: Consumables associated with biofiltration

Consumable	Amount	Comments
Filter material ([1])	NI	—
Chemicals (nutrients, alkali and acidic compounds for pH correction)	NI	—
Water (l/1 000 Nm^3)	5 ([2])	Used for the humidifier (the air stream is saturated with softened water). A quantity of percolate water will also be released from the filter material ([3])
Energy (kWh/1 000 Nm^3)	< 1 ([2])	Used to run the fans
Pressure drop (kPa)	0.5–2 ([2])	0.25 kPa for a coco filter ([3]) 1.5 kPa for a compost filter ([3])
([1]) The service life of filter material depends on its stress by acidification, poisoning and depletion. The filter material should be replaced periodically (every 0.5–5 years) depending on the type of packing material and the composition of the gases [176, Schenk et al. 2009]. ([2]) [11, InfoMil 1999]. ([3]) [176, Schenk et al. 2009]. NB: NI = no information provided.		

The lifespan of the organic filtering material (e.g. root wood, tree bark, peat, compost, coco material and/or mixtures of these) is primarily determined by acidification (N, S and Cl), depletion and/or poisoning and pressure drop. Sometimes, additional nutrients need to be added if the organic filtering material degrades too slowly [176, Schenk et al. 2009].

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 VOCs sent through the biofilter are biodegradable, there might be loaded filter material containing hazardous contaminants that has to be disposed of as waste (e.g. by incineration). The percolate water that is released from the filter material may contain organic residues and should be disposed of. Enclosed biofilters usually recirculate the leachate.

Operational data
The efficiency of biofiltration depends to a great extent on the composition of the waste gas stream. Also, sudden changes in biofilter media conditions (e.g. temperature) can adversely affect the performance of the system. If parameters do change slowly over time then the media become accustomed and efficiencies remain high [199, Fogarty and Curran 2005].

Design and maintenance [176, Schenk et al. 2009]
The typical surface pressure of a biofilter is around 50–500 Nm^3/(m^2×h), but it can drop to 5 or rise to 500 Nm^3/(m^2×h). When applying the packing, care must be taken to evenly spread the filtering material and make sure there are no tight or loose areas. These can cause short-circuit streams causing the air to be treated badly and the effective filtering surface to decrease in size. When the filter dehydrates because of short-circuit streams, the efficiency will decrease even more.

Cooling is necessary for applications with hot airflows (> 38 °C). This can be realised by a mixture of outside air, a (single-pass) water scrubber or a heat exchanger/condenser.

The filtering material should be replaced periodically (every 0.5–5 years), depending on the type of packing material and the composition of the gases.

Monitoring
Although biofilters are static in principle and require little mechanical maintenance, experience shows that regular inspection and monitoring are necessary. The abatement efficiency can be excellent during the first few years, but can decrease drastically over a short period of time

because of a lack of nutrients, problems with the fluid balance and/or the deterioration of the filter material [176, Schenk et al. 2009].

The moisture balance has to be carefully examined because it is critical 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 be abated. Regular pH examination of the percolate water released from the filter bed is required.

Applicability
Biofiltration is well-suited to low concentrations of pollutants that are easily soluble in water. It is normally not suitable, however, for waste gases 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.

[176, Schenk et al. 2009] [198, Schlegelmilch et al. 2005] When concentrations of nitrogenous, sulphurous or chlorous organic or inorganic compounds are too high, the formation of nitric acid, sulphuric acid and hydrochloric acid respectively may acidify the filtering material, rendering it useless, and thus drastically increasing the required replacement frequency. When applying biofiltration, it is important that the filtering material has a pH value in the range of 7–8 to decompose organic compounds. At a pH value of 6.5 the decomposition speed decreases. The residence time of the gas in the filter should be at least 30–45 seconds in order to properly abate odorous compounds and solvents (e.g. toluene).

Application limits and restrictions are given in Table 3.178.

Table 3.178: Application limits and restrictions associated with biofiltration

Issue	Limits/restrictions
Gas flow (Nm^3/h)	100–200 000 ([1, 2]) 100–400 per m^2 of filter surface ([3])
Temperature (°C)	15–38 ([1]) 50–60 ([1]), with thermophilic bacteria
Pressure	Atmospheric ([1])
Pressure drop (mbar)	5–20 ([1])
Oxygen content	Near ambient level ([3])
Relative humidity (%)	> 95, nearly saturated with water ([3])
Content of dust, grease and fat	Can cause clogging, hence pretreatment is necessary ([4])
VOC concentration (mg/Nm^3)	200–2 000 ([1])
Ammonia concentration (mg/Nm^3)	5–20 ([1]) Can decrease efficiency of degradation for hydrocarbons Can be degraded to N_2O
Odour concentration (ou_E/Nm^3)	20 000–200 000 ([1])
Toluene concentration (mg/Nm^3)	20–100 ([1])
Styrene concentration (mg/Nm^3)	50–500 ([1])
Hydrogen sulphide (mg/Nm^3)	5–20 ([1])
Compounds containing N, S or Cl (mg/Nm^3)	5–20 (for chlorous compounds) ([1]) Can acidify and deactivate the biofilter without buffer capacity, which brings about an increase in replacement frequency
Climatic conditions	Frost, rain and high ambient temperature affect the filter material and decrease efficiency
([1]) [176, Schenk et al. 2009]. ([2]) [227, CWW TWG 2009]. ([3]) [9, BASF 1999]. ([4]) [250, Ullmann's 2011].	

Advantages and disadvantages are given in Table 3.179.

Table 3.179: Advantages and disadvantages associated with biofiltration

Advantages	Disadvantages
• Low investment and operating costs • Simple construction • In combination with adsorption and absorption, also suitable for barely soluble compounds • High efficiency for biodegradable compounds, e.g. odorous substances • Low amount of waste water (percolate water) and waste material	• Dried-out peat and compost filter beds are difficult to rewet • Relatively bulky design • Poisoning and acidification of the biomass must be prevented • Fluctuations in the waste gas stream conditions have a significant impact on performance • Packing is sensitive to dust clogging • Limited control (including pH) • Energy consumption where cooling of the incoming gas is necessary

Economics
Economics associated with biofiltration are given in Table 3.180.

Table 3.180: Economics associated with biofiltration

Type of costs	Costs	Comments
Investment costs (per 1 000 Nm^3/h)	EUR 8 000–14 000 ([1])	—
Operating costs ([2]):	ATS 10 000–20 000 (EUR 740–1480) ([3])	—
Labour	1 h per week per filter + two days per year ([1])	—
Consumables	Water (litre/1 000 Nm^3): 5 ([1])	Strongly depends on the saturation level of the incoming gas ([1])
	Filtering material (EUR/m^3): < 200 ([1])	—
Maintenance ([4])	ATS 5 000–300 000 (EUR 370–22 000) ([3]) < ATS 1 000 (< EUR 74) ([3, 5])	—
Cost-determining parameters	Waste gas flow rate, concentration and type of pollutants, desired abatement efficiency, type and characteristics of the filter material	
Benefits	None	
([1]) [176, Schenk et al. 2009]. ([2]) Per year per 1 000 Nm^3/h capacity. ([3]) [4, Braun et al. 1994]. Average currency conversion rate for 1994: EUR/ATS = 13.53. ([4]) Per year. ([5]) Per year per 1 000 Nm^3/h capacity. NB: NI = no information provided.		

Operating and maintenance costs are generally low because no fuel or chemicals are needed. The cost of collecting and transporting the waste gas from the source to the biofilter is often more expensive than constructing the biofilter itself.

Driving force for implementation
Biofiltration is used to abate readily biodegradable compounds at relatively low concentrations in waste gases.

Example plants
The technique is reported to be used in the chemical industry sector (in particular in Germany [180, UBA DE 2009]) as well as in other sectors such as waste water treatment plants, composting facilities, the food industry, the meat processing industry, intensive livestock farming, and tobacco production and processing industries.

Reference literature
[4, Braun et al. 1994] [9, BASF 1999] [11, InfoMil 1999] [19, HMIP 1994] [104, COM 2003] [176, Schenk et al. 2009] [180, UBA DE 2009] [182, Martin 2010] [198, Schlegelmilch et al. 2005] [199, Fogarty and Curran 2005] [200, Wang et al. 1996] [227, CWW TWG 2009] [250, Ullmann's 2011]

3.5.1.3.2   Bioscrubbing

Description
Bioscrubbing combines wet gas scrubbing (absorption) (see Section 3.5.1.2.4) and biodegradation; the scrubbing water contains a population of microorganisms suitable to oxidise noxious gaseous compounds. The microorganisms are suspended in water. Hence, the conditions to use bioscrubbers are:

*   the existence of the possibility to wash out the waste gas constituents;
*   the washed-out constituents must be biodegradable under aerobic conditions.

A bioscrubber is shown in Figure 3.73.

a) Absorber
b) Activated sludge circulation
c) Activating tank

Source: [250, Ullmann's 2011]
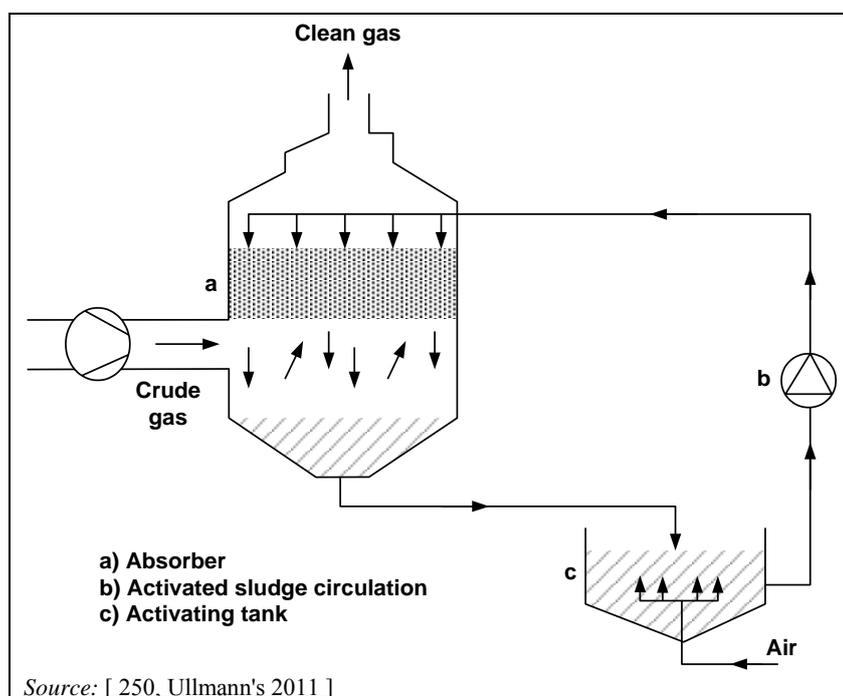
Figure 3.73: Typical bioscrubber

The bioreactor design is founded on an activated sludge or a sludge-on-carrier system (for more details see Section 3.3.2.3.5.2). 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, e.g. from 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) [11, InfoMil 1999].

A typical bioscrubbing process is shown in Figure 3.74.
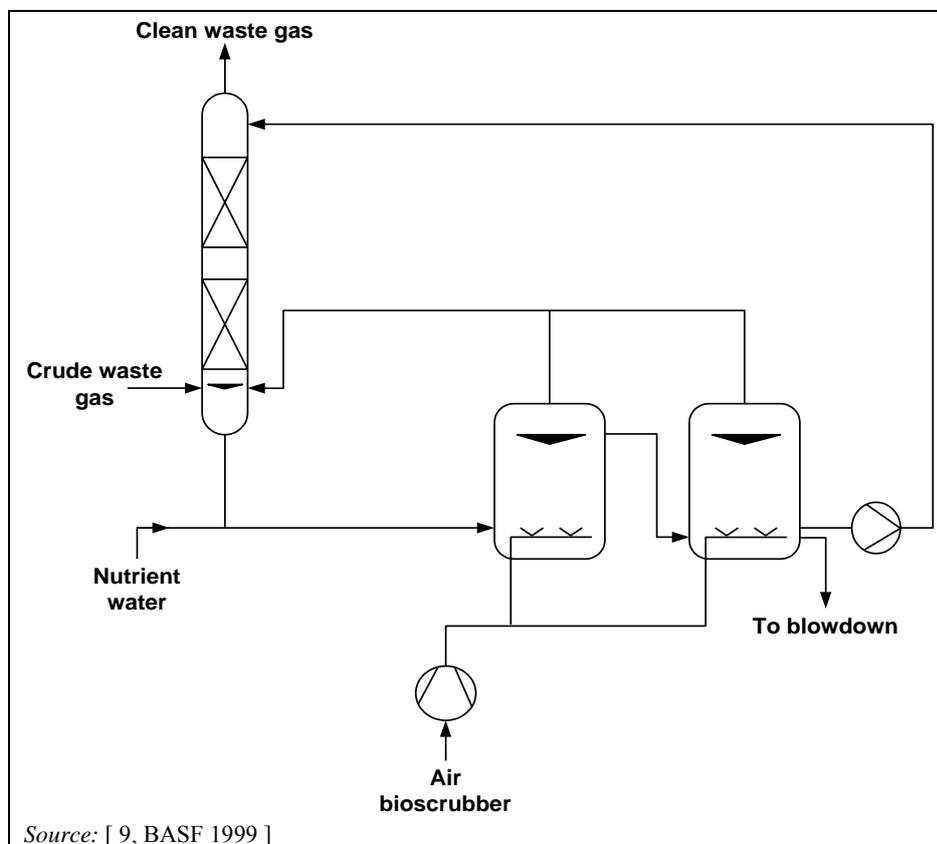
Figure 3.74: Typical bioscrubbing process

Evaporation accompanied by mineralisation and a dosage of nutrients (added to the scrubbing liquid to provide the microorganisms with lacking elements such as phosphorus, nitrogen or potassium [198, Schlegelmilch et al. 2005]) and/or neutralisation agents normally causes an increase in the salt content of 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 5 000 μS/cm [8, VDI 1996].

Measures to prevent excessive salt formation include:

*   adequate removal of absorbent and simultaneous addition of fresh water;
*   operation with softened water;
*   vapour saturation of the upstream waste gas.

Compounds which contain sulphur, chlorine and/or nitrogen lead to acidification (the 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 sufficient.

Achieved environmental benefits

Abatement efficiencies and emission levels associated with bioscrubbing are given in Table 3.181.

Table 3.181: Abatement efficiencies and emission levels associated with bioscrubbing

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm^3)	Comments
VOCs	80–90	NI	NI
Ammonia	80–95	NI	NI
Odour	70–80	100–150 ou$_E$/Nm^3	Phenols, mercaptans, H$_2$S, acetic acid and acetates contribute to the odour. Emission level reported by the tobacco industry.
([1]) Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages.			
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting.			
NB: NI = no information provided.			
Source: [176, Schenk et al. 2009].			

Cross-media effects

The main utilities and consumables are given in Table 3.182.

Table 3.182: Consumables associated with bioscrubbing

Consumable	Amount	Comments
Chemicals (nutrients, alkali compounds for pH correction)	NI	The composition and dosage of the nutrient mix is determined by the flue-gas composition. Normally, the nutrient mix consists of nitrogen, phosphorus, potassium and trace elements. ([1])
Make-up water	NI	To compensate for evaporation and drainage losses
Activated sludge	NI	—
Energy (kWh/1 000 Nm^3)	0.2–0.5 ([2])	Energy use for the recirculation pump. The bioscrubber's energy use is primarily determined by the aeration device. The size of the aeration device is determined by the load of the bioreactor, thus also the load of the air. This should be examined on a case-by-case basis. ([1])
Pressure drop (kPa)	0.2–0.5 ([2])	—
([1]) [175, VITO 2009]. [2] [176, Schenk et al. 2009]. NB: NI = no information provided.		

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, depending on the contaminants or degradation products, e.g. by incineration.

Odour might occasionally arise from the tanks storing the circulation water, so the collection of exhaust air and its subsequent ducting to a treatment facility might be necessary.

Operational data

Design and maintenance [176, Schenk et al. 2009]
The bioscrubber should be designed in such a way that the residence time of the gases is around one second. Depending on the solubility of the compounds, this may be slightly more or less. The bioscrubber requires a special open packing and special spray nozzles to prevent clogging due to the biological sludge. A hydraulic residence time of the scrubbing water of between 20 and 40 days gives the best results.

Monitoring
Efficiency is determined by chemical analysis or assessment of the odour of inlet and outlet gases. A control of the pH is required.

Applicability

Bioscrubbing is used in the chemical and petrochemical industry as well as in sewerage treatment plants. It is an abatement technique that removes readily biodegradable compounds, such as ammonia, amines, hydrocarbons, hydrogen sulphide and odorous contaminants. Bioscrubbing is well-suited to low concentrations of pollutants that are easily soluble in water.

Typical and proven applications of bioscrubbers are illustrated in Table 3.183.

Table 3.183: Typical bioscrubber applications

	Elimination of odours	Aliphatic hydrocarbons	Aromatic hydrocarbons	Oxygen-based compounds	Sulphur-based compounds	Nitrogen-based compounds	H_2S	NH_3	Ethereal oils
Activated sludge tanks of biological sewerage 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	–
Source: [8, VDI 1996]									

The applicability of bioscrubbing to different compound groups is given in Table 3.184.

Table 3.184: Applicability of bioscrubbing to compound groups

Well-suited	Generally suited	Not suited
Alcohols (methanol, ethanol, butanol, glycol, diglycol, butyl glycol) Aldehydes and ketones (formaldehyde, acetaldehyde, acetone, methyl isobutyl ketone, methyl ethyl ketone) Carboxylic acids and their esters (EDTA, acetic acid, propionic acid, butyric acid, *n*-butyl acetate, ethyl acetate, methyl methacrylate, glycolic acid ester) Phenols (phenol, cresol) Heterocyclic sulphur and nitrogen compounds Mercaptans Amines Chlorophenols Hydrogen sulphide	Naphthalene Thioethers (sulphides) Ammonia	Aliphatic hydrocarbons (methane, pentane, hexane, longer chain hydrocarbons, acetylene, cyclohexane, etc.) Aromatic hydrocarbons (benzene, toluene, xylene, styrene), except naphthalene Ethers (tetrahydrofuran, diethyl ether, dioxane) Carbon disulphide Nitro compounds Halogenated hydrocarbons (dichloromethane, trichloro-ethene, perchloroethene, 1,1,1-trichloroethane, ethylene dichloride, vinyl chloride monomer), except chlorophenols
Source: [8, VDI 1996]		

Application limits and restrictions are given in Table 3.185.

Table 3.185: Application limits and restrictions associated with bioscrubbing

Issue	Limits/restrictions
Gas flow (Nm^3/h)	1 000–3 000 Nm^3/h per m^2 of column surface ([1])
Temperature (°C)	15–40 ([2]) 30–35 (optimum) ([3])
Pressure	Atmospheric ([2])
Pressure drop (mbar)	2–5 ([4])
Sludge concentration	Maximum 15 g/l dry matter ([5])
VOC concentration in waste gas (mg/Nm^3)	100–1 000 ([4])
Concentration of ammonia	50–200 mg/Nm^3 ([2])
Silt concentration (g/l)	6–8 ([4])
Odour concentration (ou_E/Nm^3)	> 10 000 ([4])
Conductivity (µS/cm)	< 5 000 ([4])
([1]) [9, BASF 1999]. ([2]) [11, InfoMil 1999]. ([3]) [8, VDI 1996]. ([4]) [176, Schenk et al. 2009]. ([5]) [175, VITO 2009].	

Advantages and disadvantages are given in Table 3.186.

Table 3.186: Advantages and disadvantages associated with bioscrubbing

Advantages	Disadvantages
• High concentrations of easily degradable compounds can be abated owing to high microbial conversion • High concentrations of compounds containing sulphur, chlorine, and/or nitrogen can be abated by controlling the pH • Peak emissions can be controlled better than with a biofilter or biotrickling filter	• Biomass builds up, needs to be disposed of as waste and can result in blockage of the circulating water • Primarily suited for easily soluble compounds, poorly soluble compounds are more difficult to abate • Compounds must be biologically degradable • Fluctuations, e.g. changing concentrations and flow in the gas stream, have a significant impact on performance • Percolate water needs treatment
Source: [175, VITO 2009].	

Economics

Economics associated with bioscrubbing are given in Table 3.187.

Table 3.187: Economics associated with bioscrubbing

Type of costs	Costs	Comments
Investment costs (per 1 000 Nm^3/h)	EUR 6 000–20 000 (^{1})	—
Operating costs: Total (per 1 000Nm^3/h) Labour Utilities Consumables	EUR 5–10 (for 5 000 Nm^3/h) (^{2}) Half day per week (^{3}) Relatively low	—
Cost-determining parameters	Flow, type and concentration of pollutants	
Benefits	None	
(^{1}) [176, Schenk et al. 2009]. (^{2}) [175, VITO 2009]. (^{3}) [11, InfoMil 1999].		

Driving force for implementation

Bioscrubbing is used to abate low concentrations of pollutants that are easily soluble in water and readily biodegradable.

Example plants

The technique is reported to be used in the chemical industry sector as well as in other sectors such as the tobacco industry for odour removal (odour concentration is reduced from 5 000 ou$_E$/Nm^3 down to 200 ou$_E$/Nm^3), waste water treatment plants, the removal of odours arising from enzyme, aroma and polymer production, the rubber industry, the waste treatment industry, landfills for hazardous waste, intensive livestock farming, coffee-roasting houses, and slaughterhouses for odour removal.

Reference literature

[8, VDI 1996] [9, BASF 1999] [11, InfoMil 1999] [175, VITO 2009] [176, Schenk et al. 2009] [198, Schlegelmilch et al. 2005] [250, Ullmann's 2011]

3.5.1.3.3 Biotrickling

Description

Biotrickling works under similar conditions to bioscrubbing (see Section 3.5.1.3.2) but, in contrast to bioscrubbing, the microbes are fixed on supporting elements. The process is shown in Figure 3.75.
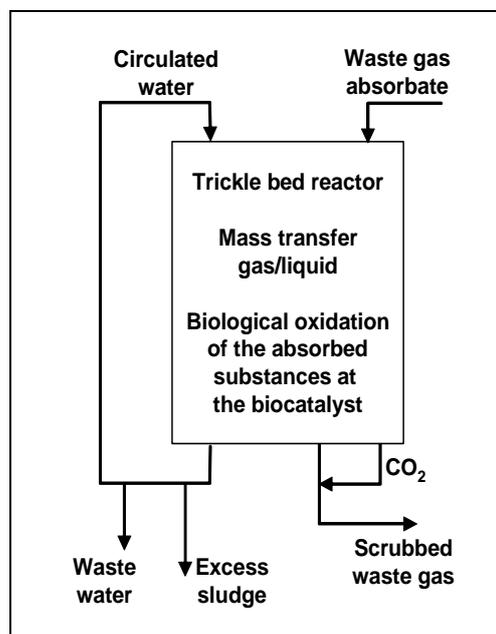
Figure 3.75: Flow sheet of the biotrickling process

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 packing. When selecting the packing material, it is necessary in every single 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 to it 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 essentially depend 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 [8, VDI 1996].

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, 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 [8, VDI 1996].

As with bioscrubbing, an increase in the salt content of the absorbent takes place. Measures to prevent excessive salt formation include:

- adequate removal of the 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 3.76.
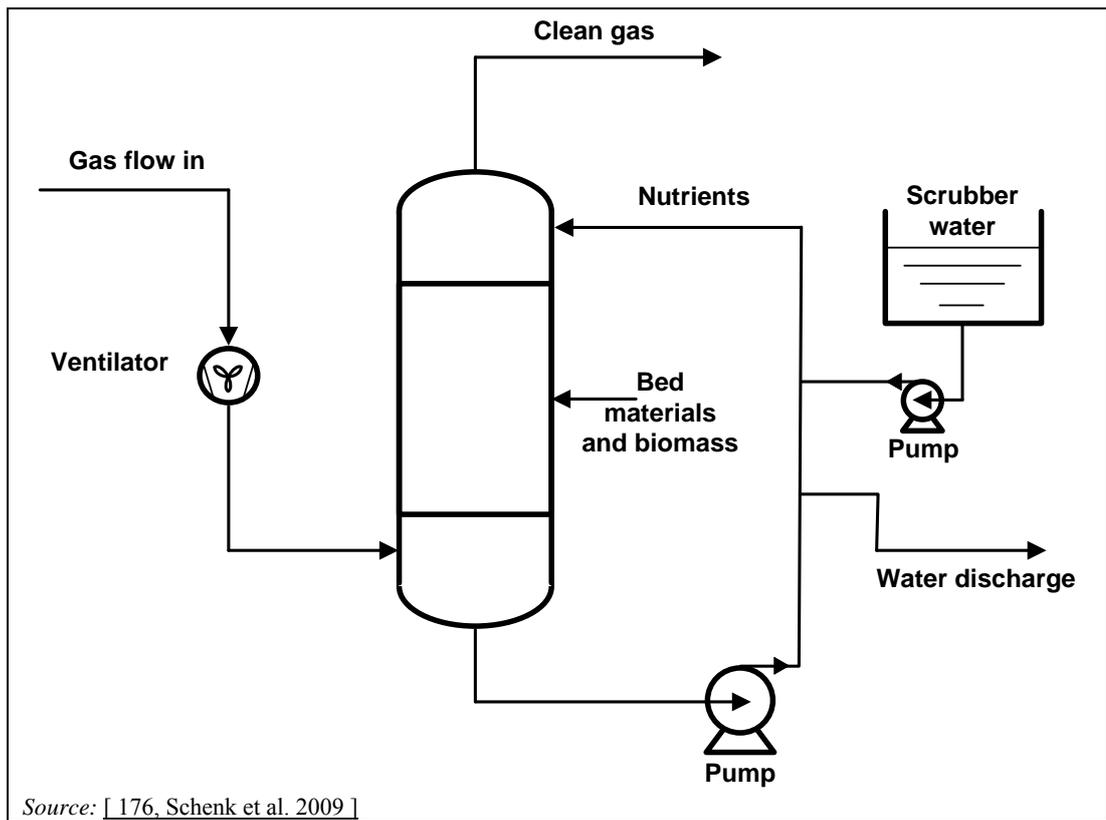
Figure 3.76: Typical biotrickling facility

Achieved environmental benefits
Abatement efficiencies and emission levels associated with biotrickling are given in Table 3.188.

Table 3.188: Abatement efficiencies and emission levels associated with biotrickling

| Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm³)	Comments
VOCs	70–99 ([3])	NI	—
Ammonia	80–95 ([3])	NI	—
Odour	70–90 ([3])	NI	—
Hydrogen sulphide	80–99 ([3])	< 1 ([3])	—
Mercaptans	70–90 ([3])	NI	—
Carbon disulphide	98–99 ([3, 4])	NI	Inlet concentration of 100 mg/Nm³
Alcohols such as ethanol, propane	90–95 ([3])	NI	Inlet concentration of 50–5 000 mg/Nm³
Ethyl acetate	70–90 ([3])	NI	Inlet concentration of 50–5 000 mg/Nm³
Toluene, xylene	70–90 ([3])	NI	Inlet concentration of 50–5 000 mg/Nm³
Styrene	80 ([3, 4])	NI	Inlet concentration of 100 mg/Nm³
Vinyl chloride monomer	99 ([3, 4])	NI	Inlet concentration of 100 mg/Nm³

([1]) Efficiency depends on the specific plant configuration and operational conditions; the performance indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].
([3]) [176, Schenk et al. 2009].
([4]) [8, VDI 1996].
NB: NI = no information provided.

Cross-media effects
The main utilities and consumables are given in Table 3.189.

Table 3.189: Consumables associated with biotrickling

Consumable	Amount	Comments
Chemicals (nutrients, alkali compounds for pH correction)	NI	—
Filtering material (synthetic foam, packing constructed from lava or plastic)	NI	—
Grafting material	NI	Depending on the type of pollutant, it may be necessary to perform grafting with a microorganism specifically bred and selected for this application. The grafting is usually done once.
Water	NI	Supplementary water to compensate for the evaporation and drainage losses
Energy (kWh/1 000 Nm³)	< 1	Value is excluding the ventilator
Pressure drop (kPa)	0.1–1	Depends on the gas load of the system and the amount of biological growth

NB: NI = no information provided.
Source: [176, Schenk et al. 2009].

Because of biological activities in the biotrickler, the salt concentration in the circulation water increases and thus should be discharged from time to time. This waste water effluent should 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, in such cases collection of exhaust air and its treatment is advised.

Operational data
Design and maintenance [176, Schenk et al. 2009]
The handling of the biological film layer (biofilm) of the packing is essential: too much growth can lead to (local) clogging that finally results in preferential streams, causing the size of the exchange surface and thus the performance of the biotrickling filter to worsen. The growth and thickness of the biofilm can be controlled by adjusting the thickness with mechanics (like varying the humidification) or by adjusting the growth of the microorganisms by varying the degree of acidity and/or the salt content. In biotrickling filters that process high H_2S concentrations, there is a chance of elementary sulphur forming because of incomplete biological oxidation. This can be recognised by the yellow granular textures and can eventually lead to clogging and preferential currents. Biotrickling filters that process high concentrations of inorganic compounds (e.g. NH_3 or H_2S) usually have microorganisms that use CO_2 from the air as a source of carbon. Given the relatively high concentrations of CO_2 in the air, extra precautions should be taken to avoid excessive growth of the biofilm.

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 pH, temperature, oxygen concentration and conductivity [8, VDI 1996].

Applicability
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 different compound groups is given in Table 3.190 (compare with the corresponding table in Section 3.5.1.3.2).

Table 3.190: Applicability of biotrickling to compound groups

Well-suited	Generally suited	Not suited
Alcohols (methanol, ethanol, butanol, glycol, diglycol, butyl glycol)	Styrene, naphthalene	Aliphatic hydrocarbons (methane, pentane)
Aldehydes and ketones (formaldehyde, acetaldehyde, acetone, methyl isobutyl ketone)	Heterocyclic sulphur compounds	Perchloroethene
Carboxylic acids and their esters (acetic acid, propionic acid, butyric acid, *n*-butyl acetate, ethyl acetate, methyl methacrylate, glycolic acid ester)	Carbon disulphide	1,1,1-trichloroethane
Phenols (phenol, cresol)	Trichloroethene, vinyl chloride monomer	
Mercaptans		
Nitrogen compounds (amines, ammonia, heterocyclic nitrogen compounds)		
Dichloromethane, 1,2-dichloroethane, chlorophenols		
Hydrogen sulphide		
Source: [8, VDI 1996]		

Application limits and restrictions are given in Table 3.191.

Table 3.191: Application limits and restrictions associated with biotrickling

Issue	Limits/restrictions
Flow (Nm^3/h)	1 000–500 000 ([1])
Temperature (°C)	15–40 ([1]) 30–35 (optimum)
Pressure	Atmospheric ([1])
Pressure drop (mbar)	1–10 ([1])
Concentration of microorganisms	> 15 g/l dry matter ([2])
VOC concentration in waste gas (mg/Nm^3)	400–4 000 ([1])
Ammonia concentration (mg/Nm^3)	100–400 ([1])
Odour concentration (ou_E/Nm^3)	> 10 000 ([1])
Hydrogen sulphide concentration (mg/Nm^3)	5–1 000 ([1])
Mercaptan concentration (mg/Nm^3)	100 ([1])
([1]) [176, Schenk et al. 2009]. ([2]) [8, VDI 1996].	

Advantages and disadvantages are given in Table 3.192.

Table 3.192: Advantages and disadvantages associated with biotrickling

Advantages	Disadvantages
• Biodegradation of absorbed compounds • Suitable for medium concentrations of acidifying compounds which contain sulphur, chlorine and nitrogen • Small pH corrections are possible • Low pressure drop • Average investment and operating costs • Compact construction and reasonable space requirements • Low energy consumption and thus limited CO_2 emissions • Little use of additives • Better reliability than a biofilter	• Fluctuations in intake air stream conditions (type and concentration of pollutants) have a significant impact on effectiveness • Poorly soluble compounds are more difficult to abate • High concentrations of toxic and acidifying substances should be prevented • The biomass can obstruct the packing • More complex to construct than a biofilter • Production of waste water, depending on the compounds abated

Economics

Economics associated with biotrickling are given in Table 3.193.

Table 3.193: Economics associated with biotrickling

Type of costs	Costs	Comments
Investment costs (per 1 000 Nm^3/h)	EUR 10 000–30 000	—

Operating costs:
    Labour
    Utilities
    Consumables
	Minimal
	4 hours per week
		Labour trongly dependent on the situation

Cost-determining parameters	Flow	
Benefits	None	
Source: [176, Schenk et al. 2009].		

Driving force for implementation
Biotrickling is used to abate low concentrations of pollutants that are easily soluble in water and readily biodegradable.

Example plants
The technique is reported to be used in the (petro)chemical industry as well as in other sectors such as waste water treatment plants (for H_2S abatement), the textile industry, the tobacco industry (to abate odours), printer shops, the wood processing industry, the metal processing industry (to abate NMVOC), the food industry, sludge-processing installations, waste-processing installations, and sewerage water pumping stations.

Reference literature
[8, VDI 1996] [176, Schenk et al. 2009]

3.5.1.3.4 Moving-bed trickling filter

Description
The moving-bed trickling filter (MBTF) is a variant of the biotrickling filter (see Section 3.5.1.3.3). The MBTF is used for the combined, or possibly separate, cleaning of air and water streams. The MBTF primarily consists of a synthetic tank. The tank is filled with 50 m^3 to 150 m^3 of specially shaped synthetic balls. On and in these grooved balls, microorganisms grow and decompose the incoming pollutants. The untreated water is pumped to the top of the reactor by an adjustable circulation pump and spread over the bed by a rotating spraying arm. The treated water is caught in the buffer/settling chamber where any sludge particles present can settle. The untreated air is blown into the reactor along with the water by an external ventilator. At the bottom, special sections of the sieve plate ensure a good separation of the air and water, after which the treated air is emitted to the atmosphere. As with any biological cleaning, part of the incoming pollutants is transformed into biomass. Thus the amount of biomass in the reactor will increase. Without precautions this will lead to clogging in conventional trickling filters. In the MBTF, clogging is prevented by pumping some of the bioballs to the top of the reactor where they will be dumped onto a sieve plate by a cyclone. A large part of the biomass on the balls is removed by the cyclone and then dropped onto the plate. The cleaned balls fall on top of the bed and can be introduced into the cleaning process again. The separated sludge is periodically disposed of.

A picture of a MBTF is shown in Figure 3.77.
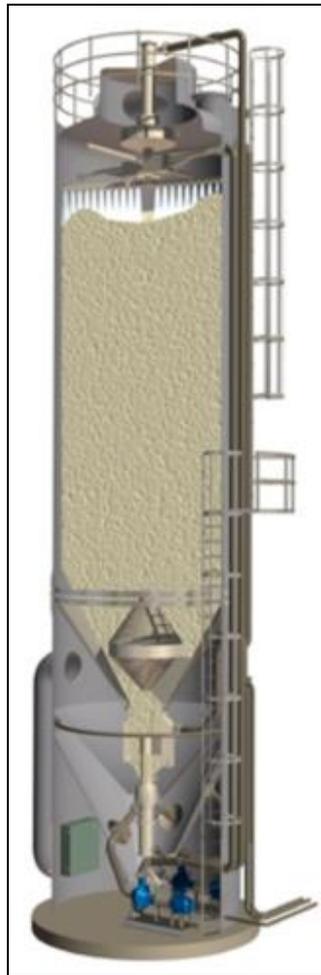
Figure 3.77: Moving-bed trickling filter

Achieved environmental benefits
Abatement efficiencies and emission levels associated with moving-bed trickling filters are given in Table 3.194.

Table 3.194: Abatement efficiencies and emission levels associated with moving-bed trickling filters

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm^3)	Comments
VOCs	80–> 95	NI	—
Odour	> 90 ([3])	> 2 500 ou$_E$/Nm^3 ([3])	Emission level reported from a chemical plant
Hydrogen sulphide	> 98	NI	—
Mercaptans	> 95	NI	—
Styrene	> 90	NI	—

([1]) Efficiency depends on the specific plant configuration, and operational conditions; the performances indicated are based upon half-hourly averages.

([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting.

([3]) The minimum odour concentration at which 90 % has been met was 2 500 ou$_E$/Nm^3. For this specific chemical plant, the maximum influent concentration has not been fixed at the time of reviewing this document (January 2011). At full scale, the MBTF has been applied for flows containing odour concentrations of approximately 2 106 ou$_E$/Nm^3. For low inlet odour concentrations, a removal efficiency of 90 % cannot be reached simply because of the odour emissions from the MBTF unit itself as it generates its own odour in the same way as any biological system does.

NB: NI = no information provided.

Source: [176, Schenk et al. 2009]

Cross-media effects
The main utilities and consumables are given in Table 3.195.

Table 3.195: Consumables associated with moving-bed trickling filters

Consumable	Amount	Comments
Nutrients	NI	Only necessary if they are not present in the waste water
Chemicals	NI	—
Water	NI	Without the treatment of waste water, additional water is needed for the removal of the remaining compounds (e.g. chloride and sulphate) and compensation of evaporation losses. In such cases, surface water can be used
Energy (kWh/1 000 Nm^3/h)	< 1–5	Varies widely; primarily determined by the ventilator
Pressure drop (mbar)	~ 40	—

NB: NI = no information provided.

Source: [176, Schenk et al. 2009].

The sludge produced should be disposed of. The drained water is already cleaned.

Operational data

Design and maintenance
The MBTF is primarily dimensioned for the waste input (air and water) and the airflow. Typical design values include [176, Schenk et al. 2009]:

- COD load: 10–20 kg/(m^3×d);
- gas load: 200–2 000 Nm^3/(m^3×h).

For the treatment of gas streams that contain compounds that are not easily soluble in water, the design should include a much higher recirculation capacity. In practice, the MBTF is filled with about 80 % of the designed volume. After starting, the system could be additionally loaded. Eventual additions to the carrying construction are always possible. Maintenance is restricted to pumps, etc. [176, Schenk et al. 2009].

Monitoring
The effectiveness of the MBTF 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 pH, temperature, oxygen concentration and conductivity.

Applicability
Application limits and restrictions are given in Table 3.196.

Table 3.196: Application limits and restrictions associated with moving-bed trickling filters

Issue	Limits/restrictions
Waste gas flow (Nm^3/h)	5 000–40 000
Waste water flow (m^3/h)	< 200
Temperature (°C)	10–45
Pressure	Atmospheric
Pressure drop (mbar)	1–10
Dust concentration	No restrictions
VOC concentration (mg/Nm^3)	100–10 000
Odour concentration (ou$_E$/Nm^3)	> 10 000
Hydrogen sulphide concentration (mg/Nm^3)	10–500
Styrene concentration (mg/Nm^3)	< 200 at 500 Nm^3/(m^2×h) < 500 at 200 Nm^3/(m^2×h)
Source: [176, Schenk et al. 2009]	

Advantages and disadvantages are given in Table 3.197.

Table 3.197: Advantages and disadvantages associated with moving-bed trickling filters

Advantages	Disadvantages
• Combined or separate treatment of waste water and waste gas is possible, leading to a compact installation • Can handle very large loads • Free of clogging • Suited for gas streams with very fast and large variations in concentration • Barely sensitive to acidification when processing nitrogen, sulphur or chlorine compounds	• Investment costs depend to a great extent on the prices of raw materials • Less suited for small gas streams (< 5 000 Nm^3/h). No limitation when processed simultaneously with waste water • Construction height up to 20 m

Economics
Economics associated with moving-bed trickling filters are given in Table 3.198.

Table 3.198: Economics associated with moving-bed trickling filter

Type of costs	Costs	Comments
Investment costs (per 1 000 Nm^3/h)	EUR 20 000–50 000	–
Operating costs: Labour Utilities Consumables	Small 1–2 hours per week	–
Cost-determining parameters	Waste load, airflow	
Benefits	Simultaneous cleaning of air and water leads to significant economic savings. The payback time is typically around 2–3 years.	
Source: [176, Schenk et al. 2009].		

Driving force for implementation
The technique is used for the combined cleaning of air and water streams mainly contaminated with organic substances that are soluble in water.

Example plants
The technique is reported to be used in the (petro)chemical industry sector as well as in other sectors such as waste processing and the meat and fish processing industry.

The technique is used in the poultry processing industry (Plusfood – Oosterwolde, NL) and at a WWTP (VED Milieu – Dronten, NL).

Reference literature
[176, Schenk et al. 2009]

3.5.1.3.5 Thermal oxidation

Description
Thermal oxidation (also often referred to as 'incineration', 'thermal incineration' or 'oxidative combustion') 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 autoignition point in a combustion chamber and maintaining it at a high temperature for sufficient time to complete combustion to carbon dioxide and water. The combined incineration of liquid waste and waste gases is dealt with in Section 3.5.3.

After thermal oxidation, the main constituents of the treated waste gas are water vapour, nitrogen, carbon dioxide and oxygen. Depending on the pollutant content of the raw waste gas being incinerated and on the operating conditions of the thermal oxidiser, other pollutants may be present in the treated waste gas such as CO, HCl, HF, HBr, HI, NO_X, SO_2, VOCs, PCDDs/PCDFs, PCBs, and heavy metal compounds (among others). It may require upstream treatment depending on the raw waste gas composition or additional downstream treatment of the treated waste gas (see Sections 3.5.1.2.4 and 3.5.1.5). Depending on the combustion temperatures during the main stages of incineration, volatile heavy metals and inorganic compounds (e.g. salts) are totally or partially evaporated. These substances are transferred from the input waste to both the treated waste gas and the fly ash it contains. A mineral residue fly ash (dust) and heavier solid ash (bottom ash) are created.

This section provides an overview of thermal oxidation in the chemical industry sector as a technique to treat waste gases, and more particularly waste gases mainly loaded with VOCs. More general information on thermal oxidation can be found in the Waste Incineration (WI) BREF [108, COM 2006].

Time, temperature (about 200–400 °C above autoignition), 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.

Normally there is only negligible dioxin formation with the combustion of waste gas streams. However, when halogenated VOCs are present, special conditions might be needed to suppress the generation (or de novo synthesis) of dioxins/furans (PCDDs/PCDFs). These special conditions (which are indicated in Chapter IV of Directive 2010/75/EU on industrial emissions [5, Directive 2010/75/EU 2010]) include:

- temperature > 1 100 °C (850 °C when incinerating waste with less than 1 % of halogenated, organic substances);
- residence time > 2 s;
- oxygen content > 3 %.

In addition, conditions that favour the formation of dioxins/furans immediately following combustion are to be prevented. This is achieved by a 'fast-quench' of post-combustion gases by cooling them very quickly from high temperatures to below the temperature window of dioxins/furans' reformation.

These measures are designed to keep PCDD/PCDF emissions below 0.1 ng TEQ/Nm³. In the case of the combustion of halogenated VOC substances, an HCl scrubber is necessary.

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 flue-gas.
- The **regenerative thermal oxidiser**, using the following steps [250, Ullmann's 2011]:
  ◦ waste 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 almost to oxidation temperature;
  ◦ then entering the combustion chamber, which is maintained at 800–1 000 °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 reused for preheating the next cycle;
  ◦ releasing the clean gas stream through an outlet valve to discharge.

Due to the relatively high combustion space temperature, the large excess of air and the small influence of the flame, only small amounts of carbon monoxide and NO_X are formed.

This system is particularly suitable for waste gas streams with flow rates in the range of 5 000–10 000 Nm^3/h. Generally, 90–97 % heat recovery (waste gas preheating) is achieved [250, Ullmann's 2011].

Examples of regenerative thermal oxidation systems are schematically given in Figure 3.78.
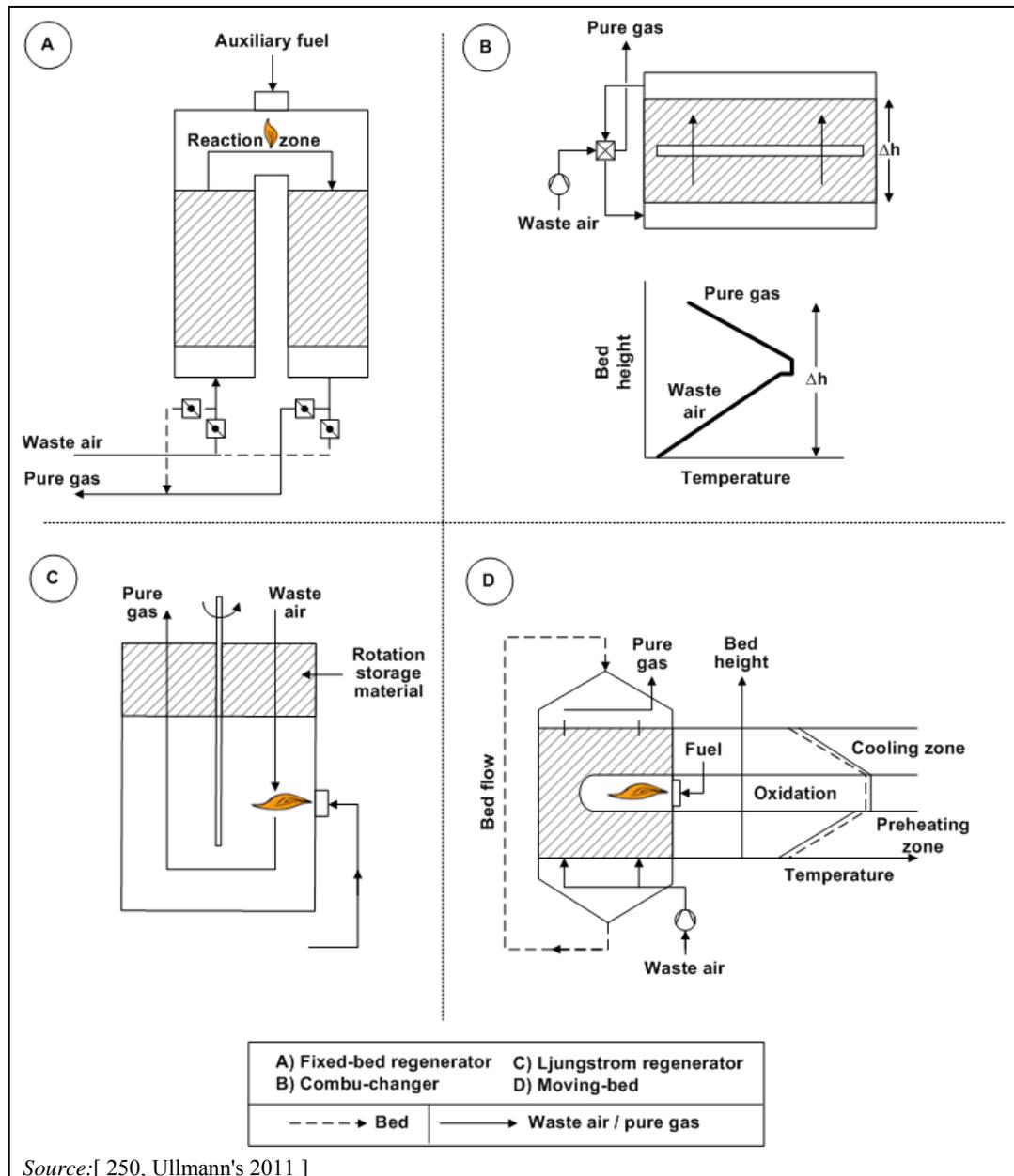
Figure 3.78: Schemes of various regenerative combustion systems

- 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 stream flow rates in the range of 1 000–50 000 Nm^3/h. Generally, 50–80 % heat recovery is achieved [250, Ullmann's 2011].

- **Gas engines and/or steam boilers** [68, UBA AT 2000], with 57–67 % energy recovery. The waste gas is burnt in the engine. The concentration of the inlet gas has to be controlled to ensure that it is burnt efficiently in the engine. If necessary, natural gas can be added as support fuel or the waste stream may need to be diluted. Downstream generators produce electricity. The engine contains a catalytic converter, principally to oxidise the carbon monoxide in the gas stream. The engine is coupled with a steam boiler to use the waste heat of the flue-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 flue-gas leaving the gas engine is led over oxidation catalysts to reduce the carbon monoxide content.

Straight thermal oxidation is a technique similar to flaring (see Section 3.5.1.6). Muffle and screen/shielded flares are, in fact, thermal oxidisers. The reason is that through their physical construction, the reaction zone is, in fact, a (semi-open or open) combustion chamber, consisting of a shielded area, with or without a controlled air supply (screen or muffle). The reaction takes place in a more controlled way, so that higher efficiencies are obtained than with other flares. Typically, the residence time exceeds one second, and a high temperature is guaranteed through the specific construction of the chamber and the supplies for waste gas streams and utilities. This type of technique can be found for both elevated or for lower-level (ground) versions [141, VITO 2009].

Muffle flares are used to treat waste gases with low to high calorific values. The minimum incineration temperature is ensured by additional fuel, the maximum temperature is restricted by airflow. Additional oxygen may be needed if the waste gas composition does not have enough oxygen. The incineration temperature is controlled [179, UBA DE 2009].

Shielded flares are used to treat waste gases with high calorific values, and which are self-flammable and capable of reaching the incineration temperature without additional fuel. The volume of excess air is self-adjusted by the aerodynamic design of the air gap around the bottom of the shield. The shield length and volume ensure the minimum residence time above the minimum temperature inside the shield under the maximum allowable flow rates. The proper operation of the pilot burner is controlled to ensure the intended incineration in the combustion chamber [179, UBA DE 2009].

Another type of enclosed burner works as a premixed surface combustion system, where premixed gas and air burns on a permeable medium. The permeable medium consists of several layers of metal fibres and withstands temperatures of up to 1 300 °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 of between 1/12 and 1/19 can be achieved. In the diffusor directly above 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 a heat exchanger an option. The enclosed combustion zone prevents discharge of heat and light [80, World Oil Magazine 2000] [94, Bekaert 2012]. The technique is shown in Figure 3.79.

Source: [80, World Oil Magazine 2000]
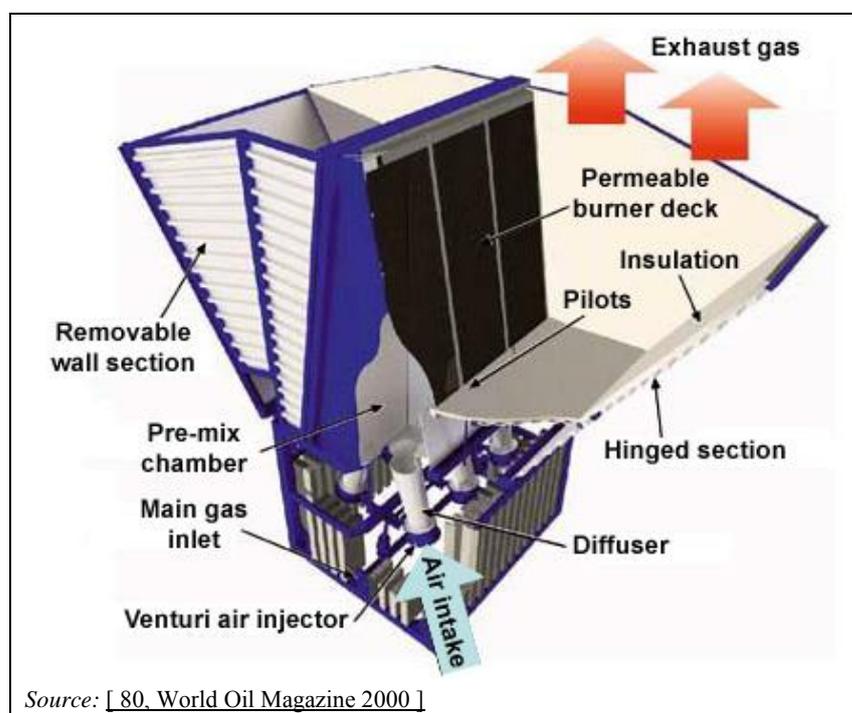
Figure 3.79: Principal components of the Clean Enclosed Burner®

Achieved environmental benefits
Abatement efficiencies and emission levels associated with straight thermal oxidation are given in Table 3.199.

Table 3.199: Abatement efficiencies and emission levels associated with straight thermal oxidation

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm³)	Comments
VOCs as TOC	98–> 99.9 ([3])	< 1–20 ([4])	Oxygen content 3 vol-%
PM₁₀	25–99.9 ([3])	NI	—
	50–99.9 ([3])	NI	—
Dust (PM size not identified)	98–99.9 ([5])	NI	—
Odour	98–99.9 ([5])	NI	—
CO	NI	39 mg/m³ ([6])	At a German incineration plant treating waste gases from three installations for a total of about 68 000 Nm³/h. The heat generated in the process is used for energy generation (combined heat and power)
NO_X as NO₂	NI	346 mg/m³ ([6])	At a German incineration plant treating waste gases from three installations for a total of about 68 000 Nm³/h. The heat generated in the process is used for energy generation (combined heat and power)

([1]) Efficiency depends on the specific plant configuration and operational conditions; unless stipulated otherwise, the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given have to be used with extreme caution for permitting [176, Schenk et al. 2009].
([3]) [55, US EPA 2003].
([4]) Low levels for hazardous substances, high levels for less hazardous substances.
([5]) [176, Schenk et al. 2009].
([6]) Daily average, 90th percentile [183, UBA DE 2009].
NB: NI = no information provided.

Abatement efficiencies and emission levels associated with regenerative thermal oxidation are given in Table 3.200.

Table 3.200: Abatement efficiencies and emission levels associated with regenerative thermal oxidation

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm³)	Comments
VOCs as TOC	95–99 ([3]) 98–99.9 ([4])	< 1–20 ([4]) ([5])	Oxygen content 3 vol-%
VOCs (predominantly carboxylic acid esters) as TOC	99.6 ([6])	13 ([7])	At a German waste gas incineration plant with a waste gas volume of 3 000 Nm³/h
PM$_{10}$	98–99.9 ([4])	NI	—
CO	98–99.9 ([4])	NI	—
Odour	98–99.9 ([4])	NI	—

([1]) Efficiency depends on the specific plant configuration and operational conditions; unless stipulated otherwise, the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given have to be used with extreme caution for permitting [176, Schenk et al. 2009].
([3]) [54, US EPA 2003].
([4]) [176, Schenk et al. 2009].
([5]) Low levels for hazardous substances, high levels for less hazardous substances.
([6]) [181, UBA DE 2009].
([7]) Daily average, 90th percentile. Organic substances as TOC in raw gas are reported to be in the range 1 600– 2 800 mg/Nm³ (30-minute arithmetic mean value) and 2 050 mg/Nm³ (daily average, 50th percentile) [181, UBA DE 2009].
NB: NI = no information provided.

Abatement efficiencies and emission levels associated with recuperative thermal oxidation are given in Table 3.201.

Table 3.201: Abatement efficiencies and emission levels associated with recuperative thermal oxidation

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm³)	Comments
VOCs as TOC	98–> 99.999 9 ([3]) 98–99.9 ([4])	< 1–20 ([4]) ([5])	Oxygen content 3 vol-%
PM$_{10}$	25–99.9 ([3])	NI	Petroleum and coal products
	50–99.9 ([3])	NI	Chemical and allied products
	98–99.9 ([4])	NI	—
CO	98–99.9 ([4])	NI	—
Odour	98–99.9 ([4])	NI	—

([1]) Efficiency depends on the specific plant configuration and operational conditions; unless stipulated otherwise, the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given have to be used with extreme caution for permitting [176, Schenk et al. 2009].
([3]) [53, US EPA 2003].
([4]) [176, Schenk et al. 2009].
([5]) Low levels for hazardous substances, high levels for less hazardous substances.
NB: NI = no information provided.

The efficiency of thermal oxidation to abate VOCs is higher than that of catalytic oxidation.

The heat from the thermal oxidation can be used to generate steam and electricity to be used on site or off site (cogeneration of heat and power). This is applicable when continuous waste gas flows are sent to the thermal oxidisers [183, UBA DE 2009] [184, UBA DE 2009].

Cross-media effects
The main utilities and consumables are given in Table 3.202.

Table 3.202: Consumables associated with thermal oxidation

Consumable	Amount	Comments
Fuel during start-up and non-autothermal conditions ([1])	NI	e.g. natural gas
Energy (kWh/1 000 Nm^3)	3–8 ([2, 3, 4]) (straight thermal oxidiser) 1.5–2.25 ([4]) (regenerative oxidiser)	—
Pressure drop (kPa)	1–5 ([1])	—
([1]) Autothermal range for VOCs: 1–10 g/Nm^3 ([2]). ([2]) [11, InfoMil 1999]. ([3]) [36, NOREC 2000]. ([4]) [176, Schenk et al. 2009]. NB: NI = no information provided.		

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 3.5.1.5.3). The presence of sulphur and halogens require further flue-gas treatment, e.g. water or alkaline scrubbing (see Section 3.5.1.2.4) to absorb hydrogen halides, lime injection (see Section 3.5.1.5.2) to absorb sulphur dioxide or GAC adsorption (see Section 3.5.1.2.3) 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 should be treated as well, e.g. by sedimentation (see Section 3.3.2.3.3.4) or neutralisation (see Section 3.3.2.3.2).

Operational data
Design and maintenance [176, Schenk et al. 2009]
The design criteria for a thermal oxidiser system depend mainly on the nature of the waste gas stream (i.e. chemical and physical characteristics such as particle size, composition, and also thermal characteristics such as calorific value and moisture level), which determines the combustion conditions. Some of the most important items are the following:

- The burners
  Some types of burners are described in Table 3.203 [19, HMIP 1994].

Table 3.203: Types of burner

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 for 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	Less expensive than distributed burners.
Premix 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 a pressure of 500 mm water gauge is needed, there is low turndown and a tendency to foul.
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.

- The mixing section [19, HMIP 1994]
  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 [19, HMIP 1994]
  Conditions for dimensioning the combustion chamber include:
  ◦ the 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 should be resistant to temperature and corrosion;
  ◦ it must withstand frequent expansion and contraction.

- Waste gas pretreatment [19, HMIP 1994]
  When pretreatment is necessary before entering the thermal oxidiser, the following has to be considered:
  ◦ 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 [19, HMIP 1994]
  Necessary safety procedures include:
  ◦ protection against flame flashback by devices, e.g. parallel plate flame arrestors, multiple screen flame arrestors, and/or water seals;
  ◦ implementing a burner purge period on start-up of the thermal oxidiser;
  ◦ shutting off flows in the event of flame failure;
  ◦ limiting of peak temperatures.

  Special systems for protection against explosions might be necessary depending on the type of waste gas to be incinerated [184, UBA DE 2009].

Thermal oxidisers should be inspected regularly and, if necessary, cleaned to maintain good performance and efficiency. When excess depositions occur, preventive actions have to be taken by cleaning the incoming gas before it enters the oxidiser. Experience with recuperative oxidisers shows that the warm side of the welds of the heat exchangers may fail, causing the

maintenance costs to increase. There are companies that changed to regenerative oxidisers for this reason. [176, Schenk et al. 2009]

Monitoring [19, HMIP 1994]
Monitored parameters which should trigger an alarm when set values are exceeded include:

- combustion temperature;
- concentration of VOCs;
- 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 VOCs and/or odour before and after the thermal oxidiser. Operational conditions on site are usually recorded to confirm that the abatement efficiency determined corresponds to normal operating conditions. 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 using GC/MS. Abatement efficiencies for odorous emissions are determined by taking grab samples at an appropriate sampling point and subsequently analysing them by olfactometry. In that case, VOC concentrations during odour sampling (according to EN 13725) should also be taken because they give information on temporal emission variability.

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.

Applicability
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 large fluctuations require the use of a flare (see Section 3.5.1.6). 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 VOCs from a wide variety of industrial processes, such as:

- the storing and loading/unloading of volatile organic liquids;
- vessel cleaning (rail tank cars, road tankers, and barges);
- venting of processes 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 are given in Table 3.204 [11, InfoMil 1999].

Table 3.204: Application limits and restrictions associated with thermal oxidation

Issue	Limits/Restrictions
Typical gas flows (Nm³/h)	900–86 000 (straight and regenerative thermal oxidiser) ([1, 2]) 90–86 000 (recuperative thermal oxidiser) ([3])
Temperature (°C)	750–1 000 ([4]) (depending on the type of pollutant ([5])) 980–1 200 with hazardous compounds ([1, 2, 3])
Pressure	Atmospheric ([5])
Pressure drop (mbar)	10–50 ([5])
VOC concentration in waste gas	< 25 % LEL ([1, 2, 3])
Dust concentration in waste gas	< 3 ([5])
Residence time (s)	0.5–2 ([6]) (dependent on temperature)
Substances	No substances that can generate corrosive compounds when gas engines or steam boilers are used
([1]) [55, US EPA 2003]. ([2]) [54, US EPA 2003]. ([3]) [53, US EPA 2003]. ([4]) [250, Ullmann's 2011]. ([5]) [176, Schenk et al. 2009]. ([6]) [9, BASF 1999].	

Advantages and disadvantages are given in Table 3.205.

Table 3.205: Advantages and disadvantages associated with thermal oxidation

Advantages	Disadvantages
• Good and constant performance • Simple principle • Reliable in operation • Recuperative and regenerative oxidation have a high thermal efficiency, with the effect of lowering extra fuel consumption and hence lowering 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 which contain sulphur and/or halogens • Additional fuel needed, at least for start-up operations, and VOC concentration below auto-ignition point (not cost-effective with low concentrations and high flow)

Economics
Economics associated with the thermal oxidation are given in Table 3.206.

Table 3.206: Economics associated with thermal oxidation

Type of costs	Costs		
	Straight	**Regenerative**	**Recuperative**
Investment costs (per 1 000 Nm³/h)	NI	USD 24 000–89 000 (EUR 25 600–95 100) ([1])	NI
	EUR 10 000–40 000 ([2])	EUR 20 000–40 000 ([2, 3])	EUR 10 000–50 000 ([2])
Annual operating costs (per 1 000 Nm³/h)	USD 24 000–45 000 (EUR 25 600–48 100) ([4])	USD 2 400–5 900 (EUR 2 560–6 300) ([1])	USD 2 800–14 800 (EUR 2 990–15 800) ([5])
	NI	FIM 6 500 (EUR 1 100) ([6])	NI
Labour Utilities Consumables (per year per 1 000 Nm³/h)	2 days per year ([3]) NI EUR 24 000–45 000 ([7])	2 days per year NI NI	5 days per year ([3]) NI NI
Cost-effectiveness (per tonne of pollutant per year)	USD 440–3 600 (EUR 470–3 850) ([4])	USD 110–21 000 (EUR 120–22 400) ([1])	USD 110–2 200 (EUR 120–2 350) ([5])
Cost-determining parameters ([8])	Waste gas flow rate, heat content of waste gases, combustion temperature (influences construction material), required removal efficiency, type of catalyst, instrumentation, heat recovery options, installation requirements (indoor, outdoor, ground level, rooftop etc.).		
Benefits	Benefits are derived if energy is recovered or if heat or electricity is produced		

([1]) Cost data for 2002 [54, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([2]) [11, InfoMil 1999].
([3]) [176, Schenk et al. 2009].
([4]) Cost data for 2002 [55, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([5]) Cost data for 2002 [53, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([6]) [36, NOREC 2000]. Fixed currency conversion rate from January 1999 onwards: EUR/FIM = 5.946.
([7]) Potentially needed for additional fuel [176, Schenk et al. 2009].
([8]) [20, HMIP 1994].
NB: NI = no information provided.

Kilns and boilers can be used for the thermal oxidation of VOCs if the temperature and residence time are in the correct range. This can be an attractive option when the kiln or boiler is already on site.

Driving force for implementation
A driver for the use of thermal oxidisers is the reduction of VOC emissions with moderate to high VOC loadings when there are minor fluctuations in flow (excess fluctuations require the use of a flare).

Example plants
The technique is reported to be widely used to abate odour and total organic compounds (TOC) in practically all industrial sectors.

Central incineration plants (i.e. treating waste gases from several installations) are in operation at several chemical plants in Germany [183, UBA DE 2009] [184, UBA DE 2009] [185, UBA DE 2009] [186, UBA DE 2009] [187, UBA DE 2009] [188, UBA DE 2009] [192, UBA DE 2009].

Reference literature
[5, Directive 2010/75/EU 2010][108, COM 2006] [9, BASF 1999] [11, InfoMil 1999] [19, HMIP 1994] [20, HMIP 1994] [36, NOREC 2000] [53, US EPA 2003] [54, US EPA 2003] [55, US EPA 2003] [68, UBA AT 2000] [80, World Oil Magazine 2000] [94, Bekaert 2012] [141, VITO 2009] [176, Schenk et al. 2009] [179, UBA DE 2009] [181, UBA DE 2009] [183, UBA DE 2009] [184, UBA DE 2009] [185, UBA DE 2009] [186, UBA DE 2009] [187, UBA DE 2009] [188, UBA DE 2009] [191, UBA DE 2009] [192, UBA DE 2009] [250, Ullmann's 2011]

3.5.1.3.6   Catalytic oxidation

Description
Catalytic oxidisers operate in a very similar way to thermal oxidisers (see Section 3.5.1.3.5), with the main difference being 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 3.80.

Source: [19, HMIP 1994]
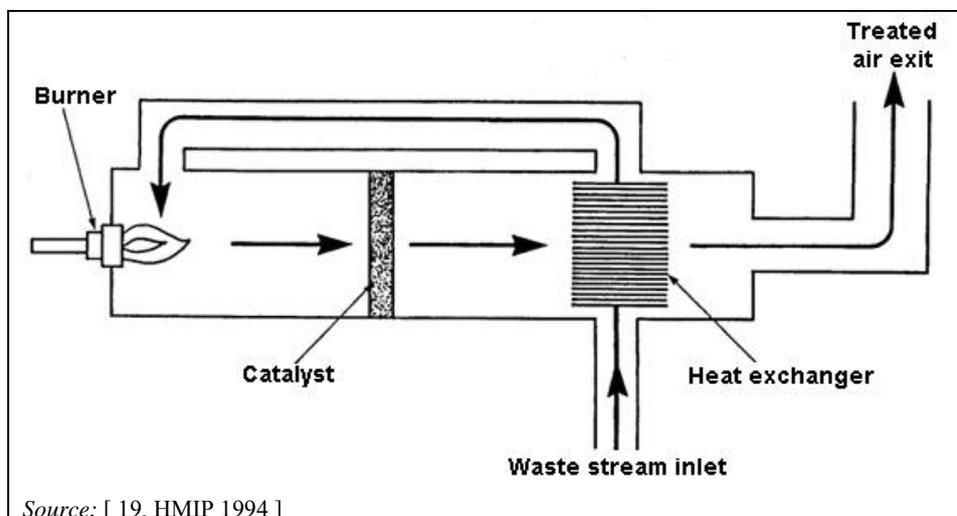
Figure 3.80: Principle of catalytic oxidation

The waste gas is heated by auxiliary burners to approximately 300–500 °C before entering the catalyst bed. The maximum design waste gas temperature of the catalyst is typically 500–700 °C [51, US EPA 2003]. There are low-temperature catalysts that work at temperatures of 200–250 °C [176, Schenk et al. 2009].

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 a 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 the high bed-side heat transfer 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 catalysts 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 which contain chlorinated compounds. Platinum-based catalysts are active for the oxidation of sulphur-containing VOCs, 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 include:

- fast-acting inhibitors, such as phosphorus, 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 the erosion of catalysts at a rate dependent on particle size, grain loading and gas velocity [20, HMIP 1994].

As with thermal oxidation (see Section 3.5.1.3.5), several types of oxidisers are used:

- the straight catalytic oxidiser;
- the regenerative catalytic oxidiser;
- the recuperative catalytic oxidiser.

Normal operating conditions for catalytic oxidisers include:

- natural gas as the preferred fuel (when additional fuel is needed);
- a distributed burner as a suitable burner;
- chambers constructed of stainless steel or carbon steel;
- a burner section with a sufficient length to provide an 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 back mixing;
- a typical residence time of 0.3–0.5 seconds.

As with thermal oxidation (see Section 3.5.1.3.5), some waste gas pretreatment can be necessary, such as condensing the water vapour from a wet waste gas, the removal of solids and liquids and – typical for the catalytic system – the removal of catalyst poisons. The safety requirements are almost the same as for thermal oxidation (see Section 3.5.1.3.5).

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 3.81.

1) Exhaust inlet
2) Bed of ceramic heat-sink material
3) Catalyst layer
4) Combustion chamber
5) Exit layer of the catalyst
6) Regenerative chamber
7) Outlet manifold
8) Transition duct

Source: [250, Ullmann's 2011]
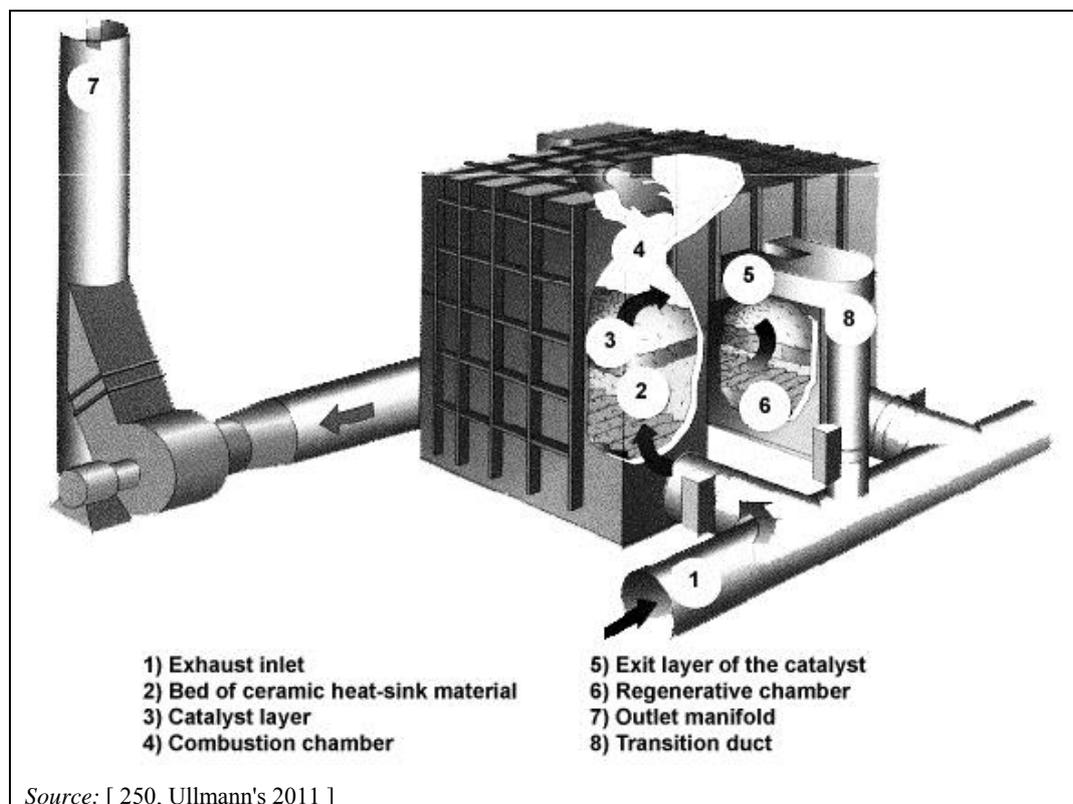
Figure 3.81: Regenerative catalytic oxidiser

Achieved environmental benefits
Abatement efficiencies and emission levels associated with catalytic oxidation are given in Table 3.207.

Table 3.207: Abatement efficiencies and emission levels associated with catalytic oxidation

Pollutant	Abatement efficiency ([1]) (%)			Emission level (mg/Nm^3)	Comments
	Straight	**Regenerative**	**Recuperative**	NI	
VOC	95 ([2])	90–99 ([3])	NI	NI	─
	98–99 ([2, 4])	NI	NI	NI	─
	95–99 ([5, 6])			< 1–20 ([5, 6])	Type of oxidiser not specified
PM$_{10}$	25–99.9 ([2])	NI	NI	NI	Petroleum and coal products
	50–99.9 ([2])	NI	NI	NI	Chemical and allied products
	< 99 ([5, 6])			NI	Type of oxidiser not specified
CO	NI	> 98 ([6, 7])	NI	NI	─
Odour	80–95 ([5, 6])			NI	Type of oxidiser not specified

([1]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].
([2]) [51, US EPA 2003].
([3]) [54, US EPA 2003].
([4]) Require larger catalyst volumes and/or higher temperatures.
([5]) Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([6]) [176, Schenk et al. 2009].
([7]) Precious metal-based catalyst.
NB: NI = no information provided.

Cross-media effects
The main utilities and consumables of the technique are given in Table 3.208.

Table 3.208: Consumables associated with catalytic oxidation

Consumable	Amount
Fuel during start-up and non-autothermal conditions (^{1}) (Nm^3 methane per 1 000 Nm^3)	0–100
Energy (kWh/1 000 Nm^3)	1–2 (^{2})
Pressure drop (kPa)	1–5 (^{2})
(^{1}) Autothermal range for VOCs: 1–2 g/Nm^3 (^{2}) (regenerative system) and 3–5 g/Nm^3 (recuperative system). (^{2}) [11, InfoMil 1999].	

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 expected. These have to be abated with suitable techniques.

Operational data
Design and maintenance [176, Schenk et al. 2009]
Catalytic oxidisers should be inspected regularly, and, if necessary, cleaned to maintain good performance and efficiency. When excess depositions occur, preventive actions should be taken by (partially) cleaning the incoming gas before it enters the oxidiser.

Monitoring [19, HMIP 1994]
The catalyst bed temperature, the pressure drop across the catalyst bed, the combustion temperature and the carbon monoxide and oxygen content of the effluent gas stream should be monitored to maintain optimal combustion conditions.

The abatement efficiency of the system may be determined by monitoring the concentration of VOCs and/or odour before and after the oxidiser. VOCs can be measured as total carbon, using a flame ionisation detector. A qualitative analysis of emissions can be done by taking grab samples at selected sampling points and by subsequently analysing them using 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 should 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.

Applicability
Catalytic oxidation is used to reduce emissions from a variety of stationary sources. The main emission source is VOCs from solvent evaporation, and catalytic oxidation is widely used by many industry sectors in this category. Examples from the chemical and related sectors are:

- process vents in the synthetic organic chemical manufacturing industry;
- rubber products and polymer manufacturing;
- polyethylene, polystyrene and polyester resin manufacturing.

Catalytic oxidation is most suited to systems with lower waste gas volumes, when there is little variation in the type and concentration of VOCs, and where catalyst poisons or other fouling contaminants are not present. Other compounds to abate are carbon monoxide and – to a certain degree – particulates, though the latter require special operational devices.

Application limits and restrictions are given in Table 3.209.

Table 3.209: Application limits and restrictions associated with catalytic oxidation

Issue	Limits/restrictions
Typical gas flows (Nm^3/h)	1 200–90 000 (straight and regenerative catalytic oxidisers) ([1, 2, 3])
	90–90 000 (recuperative catalytic oxidiser) ([3, 4])
Temperature (°C)	300–500 before the catalyst 500–700 after the catalyst
Pressure	atmospheric ([3])
Pressure drop (mbar)	10–50 ([3])
Dust concentration in waste gas (mg/Nm^3) (PM size not identified)	< 3 ([3])
VOC concentration in waste gas	< 25 % LEL ([1])
Residence time (s)	0.3–0.5 (dependent on catalyst bed volume)
([1]) [51, US EPA 2003]. ([2]) [54, US EPA 2003]. ([3]) [176, Schenk et al. 2009]. ([4]) [53, US EPA 2003].	

Advantages and disadvantages are given in Table 3.210.

Table 3.210: Advantages and disadvantages associated with catalytic oxidation

Advantages	Disadvantages
• More compact than thermal oxidisers • Requires lower temperatures (i.e. less energy consumption required, less isolation required, lower risk of fire) 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 • Good, constant and reliable performance is 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 oxidation	• Higher investment costs than with thermal oxidation • Lower efficiency in VOC destruction than thermal oxidation • System sensitive to changes in the energy content of the waste gas • Risk of dioxin formation, when chlorinated compounds are present in the waste gas • 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

Economics

Economics associated with the use of catalytic oxidation are given in Table 3.211.

Table 3.211: Economics associated with catalytic oxidation

Type of costs	Costs		
	Straight	Regenerative	Recuperative
Investment costs (EUR per 1 000 Nm³/h)	10 000–80 000 ([1])	25 000–89 000 ([2])	10 000–50 000 ([2])
Annual operating costs: (EUR per 1 000 Nm³/h)	2 500–20 000 ([2])	3 500–12 000 ([2])	NI
Labour	3 hours per week	2 hours per week	NI
Energy (kWh/1 000 Nm³/h)	1–2 ([2])	Lower than with straight catalytic oxidation	
Consumables (catalyst)	EUR/kg 35–250 depending on the type ([4])		
Cost-effectiveness (per tonne of pollutant per year)	NI	NI	NI
Cost-determining parameters ([3])	Waste gas flow rate (influences the dimensions of the combustion chamber), heat content of waste gas (influences the design of combustion equipment, the support fuel requirement), solvent destruction efficiency required (influences space velocity and consequently the amount of catalyst required), catalyst type, instrumentation, type of heat exchanger and installation requirements (indoor, outdoor, ground level, rooftop etc.).		
Benefits	None		
([1]) [11, InfoMil 1999]. ([2]) [176, Schenk et al. 2009]. ([3]) [20, HMIP 1994]. NB: NI = no information provided.			

Driving force for implementation
The main driver to use catalytic oxidation is the reduction of VOC emissions.

Example plants
The technique is reported to be used in the chemical industry sector (e.g. production of organic chemicals, rubbers, polymers, polyethylene, polystyrene and polyester resins) as well as in other sectors such as the pulp and paper industry.

Reference literature
[11, InfoMil 1999] [19, HMIP 1994] [20, HMIP 1994] [51, US EPA 2003] [53, US EPA 2003] [54, US EPA 2003] [176, Schenk et al. 2009] [250, Ullmann's 2011]

3.5.1.3.7 Ionisation

Description
In ionisation (also referred to as direct cold plasma technique), the air or the incoming gas flow is led through a reaction chamber where it is submitted to a very strong electrical field (20–30 kV) generated by electrodes, causing ions, free electrons, radicals and other highly reactive particles to be formed. However, no notable rise in temperature takes place. The highly reactive compounds cause the decomposition and (partial) oxidation of the pollutants present in the incoming gas. The most active particles in this process are the N, O and OH radicals. They are formed of nitrogen (N_2), oxygen (O_2) and water (H_2O). If the gas flow is sent directly into the plasma reactor, it acts as an electrostatic precipitator (see Section 3.5.1.4.4) with a dust removal efficiency of > 90 %. In order to keep the reactor clean, a (self-) cleaning system should be installed. The cleaning may occur through vibration, compressed air or water. In dust-free air streams, this cleaning system is not necessary. With direct treatment, the removal of organic chemicals is possible. In the case of injection of an ionised air stream, a modification of the odour molecules occurs and, to a lesser extent, a removal of the organic load.

A schematic diagram of an ionisation system is shown in Figure 3.82.
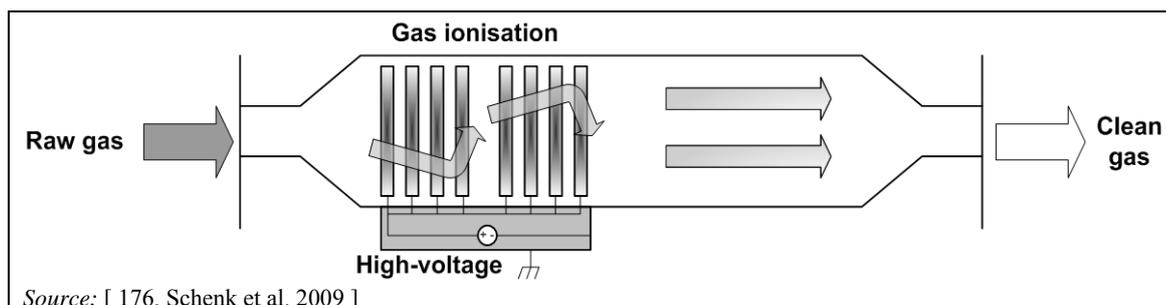
Source: [176, Schenk et al. 2009]

Figure 3.82: Ionisation system

Achieved environmental benefits
Abatement efficiencies and emission levels associated with ionisation are given in Table 3.212.

Table 3.212: Abatement efficiencies and emission levels associated with ionisation

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm^3)	Comments
VOCs	80–> 99.9	NI	Performance achieved in the wood industry
Odour	80–98	1 000–20 000 ou$_E$/Nm^3	Strongly dependent on the application and the layout of the installation (directly into the gas stream or side stream, see variants)
NO$_X$	80–95	NI	Achieved with the Low-temperature oxidation system (LoTox) variant
SO$_2$	NI	NI	—
([1]) Efficiency depends on the specific plant configuration, operational conditions; the performances indicated are based upon half-hourly averages. ([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting. NB: NI = no information provided. Source: [176, Schenk et al. 2009].			

Cross-media effects
The decomposition of VOCs can generate emissions of CO_2, H_2O_2, CO, NO$_X$, etc. which can be treated using a catalyst system [236, Bai et al. 2009].

The main utilities and consumables are given in Table 3.213.

Table 3.213: Consumables associated with ionisation

Consumable	Amount	Comments
Catalyst (if ionisation is combined with a catalyst)	NI	Lifespan around 8 000 working hours; can be regenerated
Energy (kW/1 000 Nm^3)	0.3–3	For applications in odour removal, the lower part of the range applies. The consumption is dependent on the concentration and type of compounds to be removed and the air humidity
NB: NI = no information provided. Source: [176, Schenk et al. 2009].		

Ozone created in the electrical field is a side product. If it is not completely reacted it leads to ozone emissions. Ozone has a distinctive smell and can be harmful in high concentrations. Under normal atmospheric conditions, ozone is quickly transformed into oxygen. When placing a catalyst in series after the ioniser, the ozone is completely removed. In industrial applications, the ozone emission stays below one ppm.

Waste water is emitted as a small quantity of drainage water.

When dust is present in the gas stream it needs to be disposed of as solid waste.

Operational data
Design and maintenance
The maintenance is minimal. If the unit is used to collect dust collector as well as to abate odour, a 'wash-down' once a week may be needed and an internal inspection once a month would be recommended [237, FTU 2007].

Monitoring
Voltage is the main parameter that is to be monitored.

Applicability
Ionisation is normally used to treat waste gases with low concentrations of VOCs and in cases where thermal/catalytic oxidation is not effective.

Application limits and restrictions are given in Table 3.214 [176, Schenk et al. 2009].

Table 3.214: Application limits and restrictions associated with ionisation

Issue	Limits/restrictions
Waste gas flow (Nm^3/h)	20–200 000
Temperature (°C)	20–80 Higher temperatures are possible (up to 120) with plasma oxidation
Pressure	Atmospheric
Pressure drop (mbar)	Some
Relative humidity (%)	Not too high because of risks of condensation and short-circuiting. A heightened humidity improves the performance in a side stream set-up
Dust concentration (PM size not identified)	If applied directly into the gas stream, this should include relatively low amounts of dust. The ioniser will then act as an electrostatic precipitator
Energy	Ionisation is primarily suited for gas streams with a low energy level (low concentrations of VOCs) because of the low energy consumption compared to thermal oxidisers
Source: [176, Schenk et al. 2009].	

Advantages and disadvantages are given in Table 3.215.

Table 3.215: Advantages and disadvantages associated with ionisation

Advantages	Disadvantages
• Low energy consumption compared to thermal oxidisers (for gas streams with low-energy levels) • Very compact • May be turned on and off at will (almost no start-up time) • Relatively simple operation • Not sensitive to variations in the gas stream • The ionisation process takes place at a low temperature • When operating in bypass, not sensitive to dust	• Electricity consumption • Test installation is preferred for the proper evaluation of situation-specific effects and possible removal efficiency • Only suitable for VOC removal when the system is applied directly to the gas stream • Risk of electromagnetic radiation. This risk is limited when the casing is made of metals

Economics

Economics associated with ionisation are given in Table 3.216.

Table 3.216: Economics associated with ionisation

Type of costs	Costs	Comments
Investment costs: (per 1 000 Nm^3/h)	Up to EUR 50 000 (^{1})	Strongly dependent on the application
Injector	EUR 2 600 (^{2})	—
Catalyst	Up to EUR 660 (for 8 000-hour lifespan) (^{2})	—
Operating costs: Labour Utilities Consumables	3–5 % of investment costs 1–2 man-days per year (^{1}) 0.3–3 kWh/1 000 Nm^3 (^{3})	—
Cost-determining parameters	Incoming airflow	
Benefits	None	
(^{1}) [176, Schenk et al. 2009]. (^{2}) Part of the total investment costs mentioned above [176, Schenk et al. 2009]. (^{3}) [227, CWW TWG 2009]. NB: NI = no information provided.		

Driving force for implementation

The driving force for using ionisation is the reduction of VOC (including odorous) emissions.

Example plants

The technique is reported to be used in industry sectors such as waste water treatment plants, sludge processing, slaughterhouses, the feed and food industry (in 2007, 25 cold plasma units were in operation in the pet food industry [237, FTU 2007]).

Reference literature

[176, Schenk et al. 2009] [227, CWW TWG 2009] [236, Bai et al. 2009] [237, FTU 2007]

3.5.1.3.8 Photo/UV oxidation

Description
The incoming waste gas stream is led through a reaction chamber and radiated with UV waves (100–280 nm). This radiation causes the decomposition of the undesired compounds. This decomposition takes place in two ways:

- direct photolysis: compounds such as VOCs, NH_3, H_2S and amines are directly broken down by the radiation;
- oxidation by reactive oxygen radicals: the presence of highly reactive oxygen radicals oxidises compounds that are not broken down by direct photolysis and reaction products from the photolysis.

A schematic diagram of a photo/UV oxidation system is shown in Figure 3.83.

Source: [176, Schenk et al. 2009]
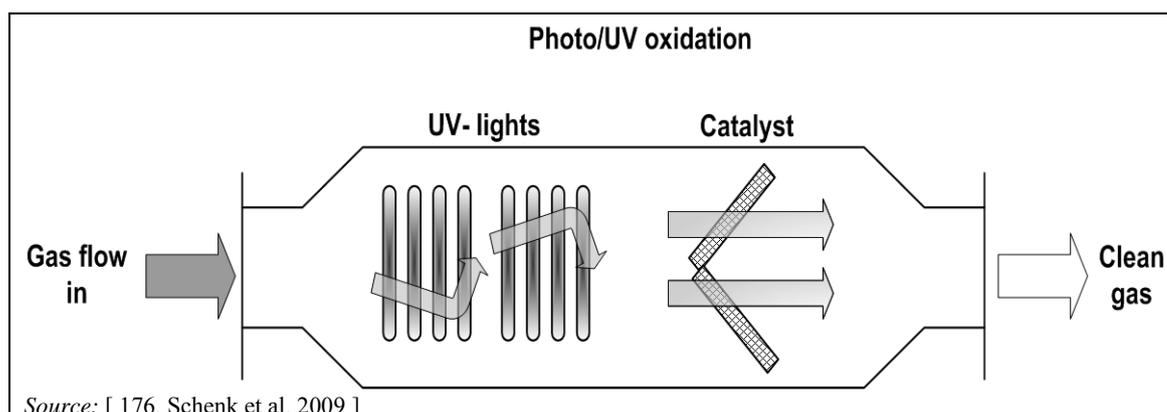
Figure 3.83: Photo/UV oxidation system

Some suppliers install a catalyst (activated carbon) or a second set of lamps with a different wavelength after the first photo oxidation phase to reach the highest possible removal rate. This extra phase also serves to break down the remaining ozone into oxygen.

Achieved environmental benefits
Abatement efficiencies and emission levels associated with photo/UV oxidation are given in Table 3.217.

Table 3.217: Abatement efficiencies and emission levels associated with photo/UV oxidation

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm³)
VOCs	95	25–50
Odour	80–98	NI
H_2S, NH_3, amines, mercaptans	< 98	NI
([1]) Efficiency depends on the specific plant configuration, operational conditions; the performances indicated are based upon half-hourly averages. ([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting. NB: NI = no information provided. Source: [176, Schenk et al. 2009].		

Cross-media effects
The treated gas could contain ozone. Under normal conditions however, ozone is quickly decomposed into oxygen. Besides spent UV lamps (expected lifespan of about 8 000 hours), no waste is created. The energy consumption is in the range of 0.3–1.5 kWh/1 000 Nm^3 [227, CWW TWG 2009].

Operational data
No information provided.

Applicability
Application limits and restrictions are given in Table 3.218 [176, Schenk et al. 2009].

Table 3.218: Application limits and restrictions associated with photo/UV oxidation

Issue	Limits/restrictions
Waste gas flow (Nm^3/h)	2 000–58 000 (in theory not very critical)
Temperature (°C)	< 60
Pressure	Atmospheric
Pressure drop (mbar)	NI
Relative humidity (%)	< 85 (max. dew point, no mist)
VOC concentration (mg/Nm^3)	< 500
H$_2$S, NH$_3$, amines, mercaptans (ppm)	< 50
Dust concentration	Dust removal should preferably be carried out
NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].	

Advantages and disadvantages are given in Table 3.219.

Table 3.219: Advantages and disadvantages associated with photo/UV oxidation

Advantages	Disadvantages
• Compact and modular system • Close to no start-up time • Operation at low temperature • Low energy consumption • Noise-free	• Not suitable for high concentrations of pollutants

Economics
Economics associated with photo/UV oxidation are given in Table 3.220.

Table 3.220: Economics associated with photo/UV oxidation

Type of costs	Costs
Investment costs (per 1 000 Nm^3/h)	EUR 5 000–7 000
Operating costs (EUR/kg VOCs abated)	3–25
Consumables (EUR/1 000 Nm^3/h): UV lamps Catalyst Energy	0.06–0.2 0.06–0.12 0.3–1.5 kWh
Cost-determining parameters	UV lamps, catalyst
Benefits	None
Source: [176, Schenk et al. 2009].	

Driving force for implementation
No information provided.

Example plants
The technique is reported to be used in industry sectors such as coating installations, waste water treatment plants, waste-processing installations, fermentation processes and the food industry.

Reference literature
[176, Schenk et al. 2009] [227, CWW TWG 2009]

3.5.1.4 Recovery and abatement techniques for particulates

3.5.1.4.1 Overview

Particulate pollutants (also referred to as particulate matter, PM) are dust, heavy metals and their compounds, aerosols, mist and soot, which can frequently be found in waste gas 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 flue-gases from combustion, e.g. power plants or waste incineration. Aerosols and mists appear, for example, during reaction and work-up of production mixtures.

Figure 3.84 provides an indicative overview of some of the techniques that can be used to recover and abate particulate matter.

Source: [176, Schenk et al. 2009]
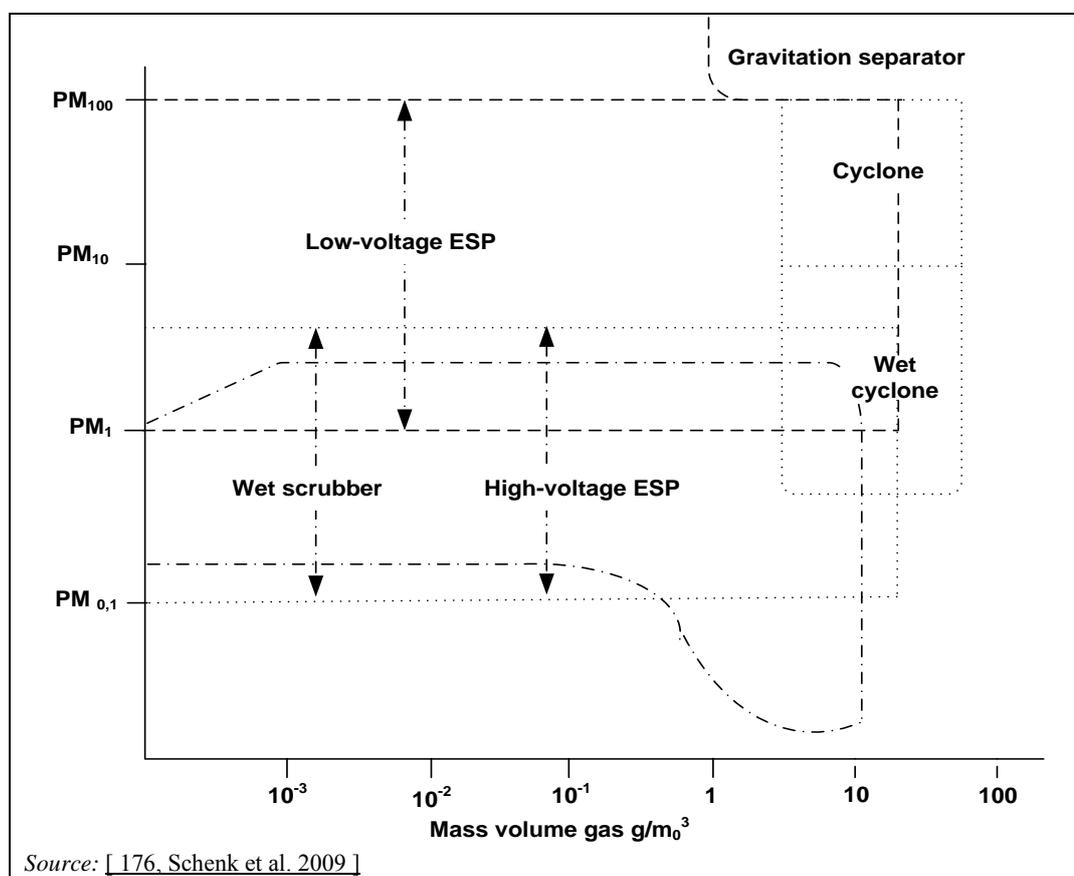
Figure 3.84: Indicative overview of some of the techniques that can be used to recover and abate (fine) particulate matter

The common treatment techniques used to recover and abate particulates are described below.

3.5.1.4.2   Settling chamber/gravitational 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 separating effect is increased by reducing the gas velocity by design means, e.g. baffles, lamellae or metal gauze (see Figure 3.85).

The design should ensure a uniform speed distribution inside the chamber. 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 the volume of the separator compared with the settling chamber. The drawback is the increasing pressure drop.

This technique is part of the group of air pollution control techniques referred to as precleaners.

Source: [176, Schenk et al. 2009]
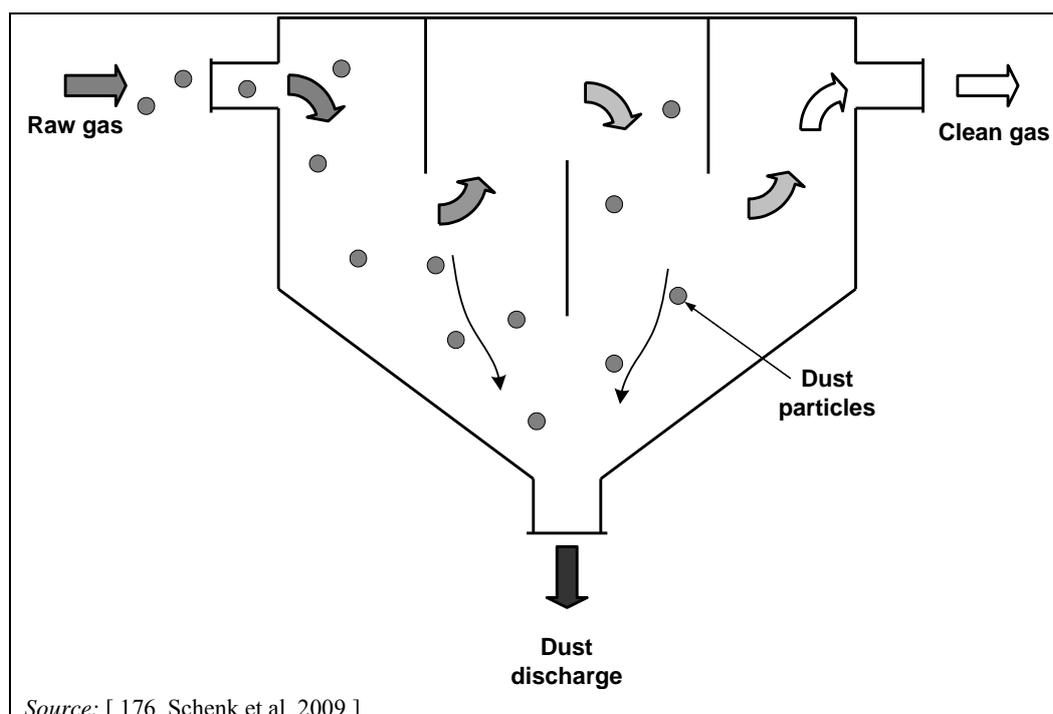
Figure 3.85: Settling chamber

Achieved environmental benefits
Abatement efficiencies and emission levels associated with settling chambers are given in Table 3.221.

Table 3.221: Abatement efficiencies and emission levels associated with settling chambers

Pollutant	Abatement efficiency(%)	Emission level (mg/Nm^3)	Comments
Dust (PM size not identified)	10–90 ([1, 2])	High; > 100 possible ([2])	Strongly dependent on PM size; large particles are better removed than small particles
Droplets	NI	100 ([1])	In demisters
([1]) [11, InfoMil 1999]. ([2]) [176, Schenk et al. 2009]; Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages. NB: NI = no information provided.			

Cross-media effects
Consumables associated with settling chambers are given in Table 3.222.

Table 3.222: Consumables associated with settling chambers

Consumable	Amount	Comments
Water (optional cleaning system for baffles or lamellae)	100–200 l/m^2	Depends on the particular application
Energy (kWh/1 000 Nm^3)	NI	Only for the fan
Pressure drop (kPa)	< 0.5	—
NB: NI = no information provided.		
Source: [11, InfoMil 1999].		

Residues are the separated dust and/or the separated droplets which have to be disposed of when reuse/recirculation is not possible. Depending on its source, the separated dust might be contaminated with toxic or hazardous contents which need to be considered for further treatment or disposal.

Operational data
Design and maintenance [176, Schenk et al. 2009]
Settling chambers may be constructed of various materials, including steel and synthetic material, depending on the composition of the waste gas stream.

In the application of settling chambers, a uniform speed distribution is essential. Preferential streams have a negative effect on the functioning of the settling chamber. By using internal obstructions, work at higher speeds can be achieved, resulting in a smaller settling chamber. The downside to this is the increase in the pressure drop of the system. Leakage of cold air into the settling chamber must be avoided to prevent condensation of the gas stream. Condensation may lead to corrosion, dust accumulation and an obstruction of the dust outlet.

Monitoring [176, Schenk et al. 2009]
The most frequently occurring cause of malfunction is obstruction of the chamber by dust. This can be prevented through constant monitoring and periodic inspections of the chamber.

Applicability
A gravitational separator is usually installed as a preliminary step in various dust filter systems, scrubbers, cooling towers, etc. It is used, for example, to prevent entrainment of the washing liquid with the purified waste gas and/or to remove hot or abrasive particles. It is not applicable to treat particulates in flue-gas.

Application limits and restrictions are given in Table 3.223.

Table 3.223: Application limits and restrictions associated with settling chambers

Issue	Limits/restrictions
Waste gas flow (Nm^3/h)	100–100 000 ([1])
PM content (g/Nm^3)	No restriction
PM size	PM$_{>10}$, better efficiency for PM$_{>50}$ ([2])
Temperature	Normally up to about 540 °C, limited by the construction materials used for the settling chamber ([2])
Pressure (bar)	No restriction ([3])
Fluid percentage	Above dew point ([3])
([1]) [11, InfoMil 1999].	
([2]) [44, US EPA 2003].	
([3]) [176, Schenk et al. 2009].	

Advantages and disadvantages are given in Table 3.224.

Table 3.224: Advantages and disadvantages associated with settling chambers

Advantages	Disadvantages
• Simple construction, no moving parts, hence low maintenance and operating costs • Very low pressure drop • Suitable for higher temperatures • Low investment costs • Low energy consumption • Can be applied to processes with large fluctuations, e.g. with high and low temperatures	• Poor removal efficiency, especially for small particles • Unsuitable for sticky particles • Not suitable when the density difference between gas and particulates is small • Relatively large equipment
Source: [176, Schenk et al. 2009].	

Economics
Economics associated with settling chambers are given in Table 3.225.

Table 3.225: Economics associated with settling chambers

Investment costs (EUR/1 000 Nm³/h)	Low if the system is integrated into other systems
Operating costs (EUR/1 000 Nm³/h)	Low
Consumables/additives	None
Energy costs (i.e. electricity)	Low (i.e. to power the fans)
Costs determining parameters	Pressure drop
Benefits	None, unless dust is recovered and reused/recycled
Source: [176, Schenk et al. 2009].	

Driving force for implementation
Reduction of particulate matter emissions as well as material recovery are the main driving forces for implementation of the technique.

Example plants
The technique is reported to be widely used in the chemical industry sector as well as in other sectors such as the wood and furniture industry, the construction sector, ceramics production, the glass industry, the storage and handling of dusty materials, and the iron and steel and non-ferrous metals industries.

Reference literature
[11, InfoMil 1999] [44, US EPA 2003] [176, Schenk et al. 2009]

3.5.1.4.3 Cyclones

Description
Cyclones use inertia to remove particles from the waste gas stream, imparting centrifugal forces, usually within a conical chamber.

Source: [176, Schenk et al. 2009]
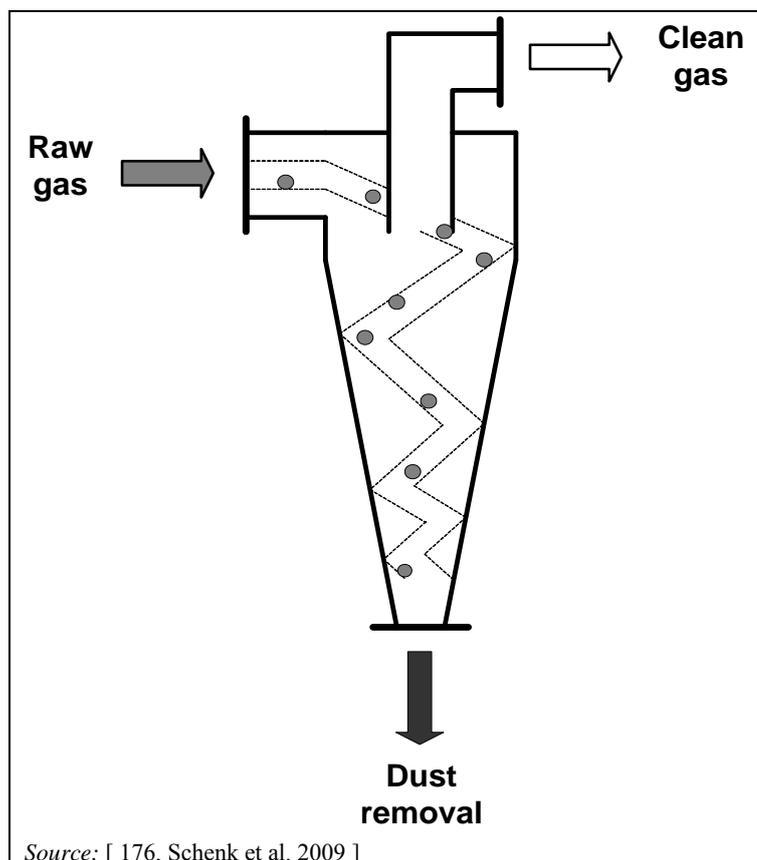
Figure 3.86: Cyclone

Cyclones 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 towards 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 and may need to be abated by other treatment techniques (e.g. scrubbers, electrostatic precipitators, fabric filters). A schematic of a cyclone is shown in Figure 3.86.

Wet cyclones are highly efficient 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: reverse flow and straight-through cyclones [19, HMIP 1994] and these are described below.

- **The reverse flow cyclone** (see Figure 3.87), which is the most common, consists of:
    ◦ a cylindrical shell with a conical base;
    ◦ a dust collection hopper;
    ◦ an air inlet, either tangential or axial;
    ◦ outlets.
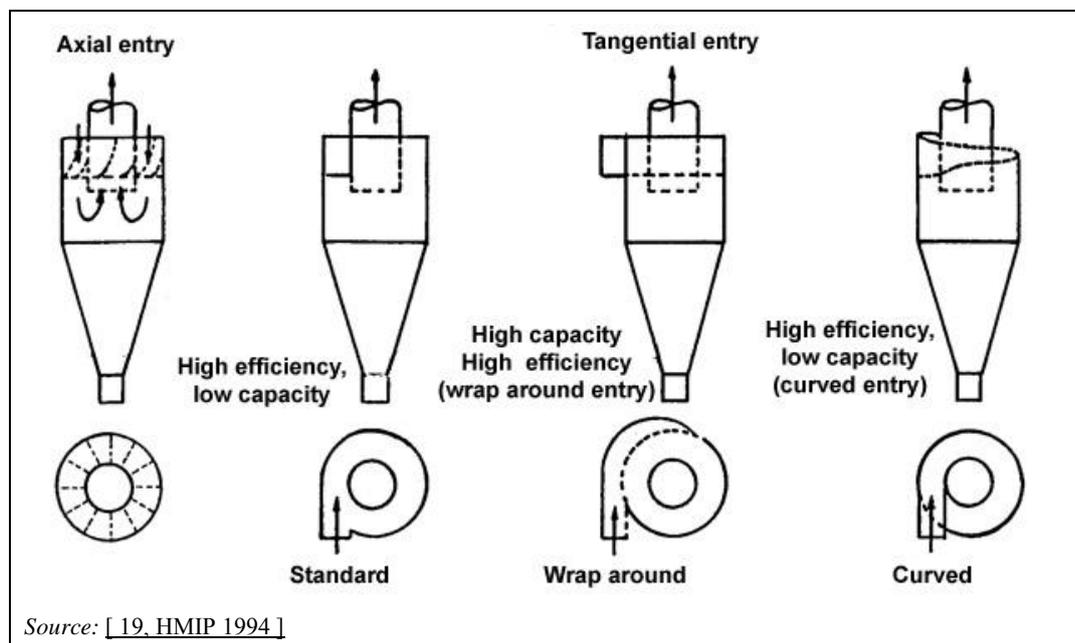
Figure 3.87: Reverse flow cyclone

- **The straight-through cyclone** (see Figure 3.88) 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.
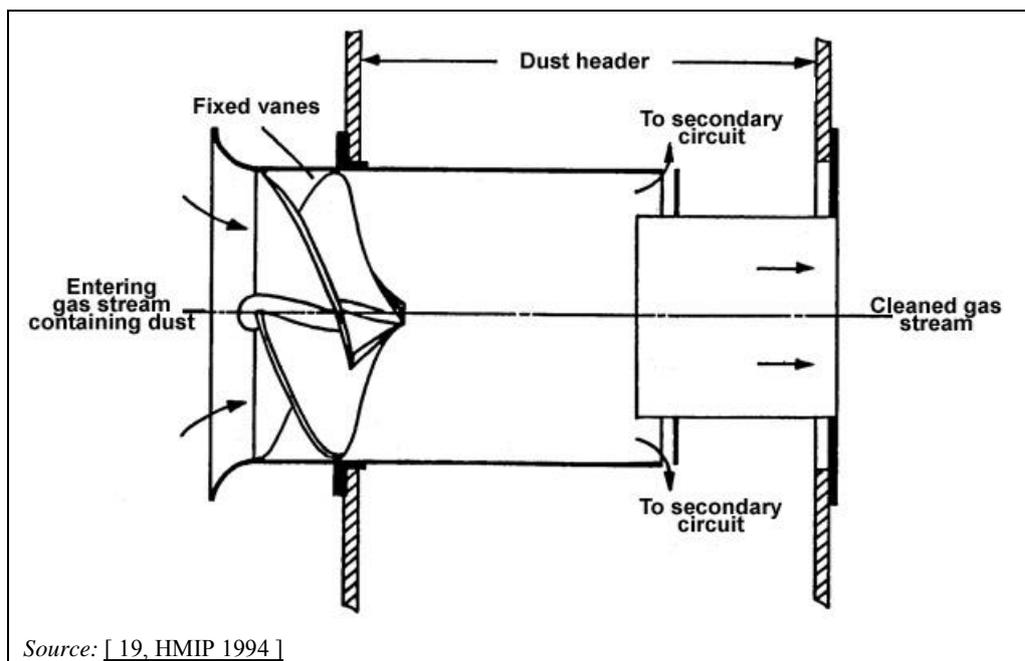
Figure 3.88: Straight-through cyclone

High-throughput cyclones have a diameter of more than 1.5 m and are suitable for the removal of particles of 20 µm and up [176, Schenk et al. 2009].

High-efficiency cyclones have a diameter that varies between 0.4 m and 1.5 m and are applicable for the removal of particles of 10 µm and up [176, Schenk et al. 2009].

Multi-cyclones are constructed in parallel out of cyclones with a diameter ranging between 0.005 m and 0.3 m. Here the gas feed occurs tangentially or axially, after which the gas is brought into rotation by blades. A multi-cyclone is sensitive to the good distribution of the gas amongst the smaller cyclones. If the distribution is wrong, a reversal or clogging of the gas may occur. Multi-cyclones can reach a high removal efficiency of over 99 %, depending on particle size [176, Schenk et al. 2009].

Achieved environmental benefits
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 [43, US EPA 2003].

The collection efficiency of cyclones varies as a function of particle size and cyclone design. It increases with [43, US EPA 2003]:

- particle size and/or density;
- inlet duct velocity;
- cyclone body length;
- the number of gas revolutions in the cyclone;
- the ratio of cyclone body diameter to gas exit diameter;
- dust loading;
- smoothness of the cyclone inner wall.

The collection efficiency decreases with [43, US EPA 2003]:

- increasing gas viscosity;
- increasing gas density;
- increasing the duct area of the gas inlet;
- leakage of air into the dust outlet.

Abatement efficiencies associated with cyclones are given in Table 3.226.

Table 3.226: Abatement efficiencies associated with cyclones

Pollutant	Abatement efficiency(%)				Comments
	Conventional	**High-efficiency**	**High-throughput**	**Multi-cyclone**	
PM$_{>50}$	99 ([1])				Type of cyclone not specified
PM$_{>10}$	90 ([1])				Type of cyclone not specified. Remaining emissions of dust 100 mg/Nm^3 ([1])
Dust (PM size not identified)	70–90 ([2])	80–99 ([2])	80–99 ([2])	NI	—
PM$_{10}$	30–90 ([2])	60–95 ([2])	10–40 ([2])	NI	
PM$_{6–10}$	50 ([1])				Type of cyclone not specified
PM$_5$	NI	90 ([2])	NI	80–95 ([2])	—
PM$_{2.5}$	0–40 ([2])	20–70 ([2])	0–10 ([2])	NI	—
PM$_{<1}$	5 ([1])				Type of cyclone not specified
([1]) [176, Schenk et al. 2009]; Efficiency depends on the specific plant configurations and operational conditions; the performances indicated are based upon half-hourly averages. ([2]) [43, US EPA 2003]. NB: NI = no information provided.					

Cross-media effects
Consumables associated with cyclones are given in Table 3.227.

Table 3.227: Consumables associated with cyclones

Consumable	Amount	Comments
Water (wet cyclones)	NI	─
Energy (kWh/1 000 Nm³)	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}) [9, BASF 1999]. (^{2}) [43, US EPA 2003]. NB: NI = no information provided.		

Dust is emitted as a residue and has to be disposed of if it cannot be reused or recycled. 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 dust slurry of a wet cyclone is treated in a waste water treatment plant.

The operation of cyclones is a significant source of noise, which has to be abated, e.g. by enclosing the equipment.

Operational data
Design and maintenance [176, Schenk et al. 2009]
Cyclones are most efficient at high air speeds, with small diameters and long cylinder lengths. The high-throughput cyclone with its high capacity and thus large size is generally not as efficient as a cyclone with lower throughput.

The air speed of a cyclone is between 10 m/s and 20 m/s and the average speed is about 16 m/s. Fluctuations in this speed (lower speed) cause the removal efficiency to drop sharply. The efficiency of a cyclone is determined by the particle size and the design of the cyclone.

The efficiency is improved when the following parameters are increased:

- particle size and density;
- cyclone length;
- circulation of the incoming gas stream in the cyclone;
- dust load;
- the smoothness of the inside of the cyclone.

The efficiency is decreased by an increase in:

- the diameter of the cyclone chamber;
- the diameter of the outgoing gas stream;
- the surface of the entry point of the incoming gas stream;
- the gas density.

Maintenance requirements for cyclones are low; there should be easy access to enable a periodic inspection of the cyclone for erosion or corrosion. The pressure drop across the cyclone is routinely monitored and the dust-catching system is checked for blockages.

Monitoring [19, HMIP 1994]
The performance level of a cyclone can be determined by monitoring the particulate concentrations in the effluent gas stream, using an isokinetic sampling probe or a meter based, for example, on UV/visible opacity, beta rays or particle impingement.

Applicability

Cyclones are used to control particulate material, and primarily PM_{10}. There are, however, high-efficiency cyclones (e.g. multi-cyclones) designed to be effective even for $PM_{2.5}$ [43, US EPA 2003].

Cyclones themselves are generally not adequate for meeting air pollution regulation limits, but they serve a purpose as precleaners for more expensive final control devices such as fabric filters (see Section 3.5.1.4.6) or electrostatic precipitators (see Section 3.5.1.4.4). 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 $PM_{2.5}$.

Application limits and restrictions are given in Table 3.228.

Table 3.228: Application limits and restrictions associated with cyclones

Issue	Limits/restrictions
Waste gas flow (Nm^3/h)	1–100 000 ([1, 2]), (single cyclone unit)
	Up to 180 000 ([2]) (multiple cyclones in parallel)
Dust content (g/Nm^3)	1–16 000 ([2])
Particulate size	$PM_{<2.5-200}$ ([2])
Temperature	Dependent on vessel material, can be > 1 200 °C ([1])
([1]) [250, Ullmann's 2011]. ([2]) [43, US EPA 2003].	

Advantages and disadvantages are given in Table 3.229.

Table 3.229: Advantages and disadvantages associated with cyclones

Advantages	Disadvantages
• Simplicity of the installation • Recovery of raw material • No moving parts, hence few maintenance requirements and low operating costs • Low investment costs • Dry collection and disposal, except for wet cyclones • Relatively small space requirements	• Relatively low PM abatement efficiency, particularly for PM_{10} • Relatively high pressure drop • 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 • Emissions to waste water with wet cyclones • Noise

Economics

Economics associated with cyclones are given in Table 3.230.

Table 3.230: Economics associated with cyclones

Type of costs	Costs	
	Single conventional cyclone	**Multiple cyclones**
Investment costs (per 1 000 Nm^3/h)	EUR 1 200 ([1])	NI
	EUR 900 ([2])	NI
Annual operating costs: (per 1 000 Nm^3/h)	EUR 200 ([2])	NI
Labour	Up to 2 hours per week	
Cost-effectiveness (per tonne of pollutant controlled per year)	NI	NI
Cost-determining parameters	Gas flow, pressure drop	
Benefits	None, unless dust material is recovered and reused/recycled	
([1]) [176, Schenk et al. 2009]. ([2]) [11, InfoMil 1999]. NB: NI = no information provided.		

For the conventional single cyclone, flow rates are assumed to be between 1 800 Nm^3/h and 43 000 Nm^3/h, PM loading between 2.3 g/Nm^3 and 230 g/Nm^3 and control efficiency to be 90 %. For the multi-cyclone, these are assumed to be between 36 000 Nm^3/h and 180 000 Nm^3/h with 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.

Driving force for implementation
Reduction of particulate matter emissions as well as material recovery are the main driving forces for implementation of the technique.

Example plants
The technique is reported to be widely used in the chemical industry sector as well as in other sectors such as the wood and furniture industry, the construction sector, ceramics production, the glass industry [115, COM 2013], the storage and handling of dusty materials, waste incineration [108, COM 2006], coffee roasting [118, COM 2006], and the iron and steel and non-ferrous metals industries.

Reference literature
[9, BASF 1999] [11, InfoMil 1999] [19, HMIP 1994] [43, US EPA 2003] [176, Schenk et al. 2009] [108, COM 2006] [115, COM 2013] [118, COM 2006] [250, Ullmann's 2011]

3.5.1.4.4   Electrostatic precipitator

Description
An electrostatic precipitator (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 a 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 ESPs:

- dry wire plate ESP,
- dry wire pipe ESP,
- wet wire plate ESP,
- wet wire pipe ESP.

In the **wire plate ESP** (see Figure 3.89), 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 3.90), the waste 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.


Source: [19, HMIP 1994]
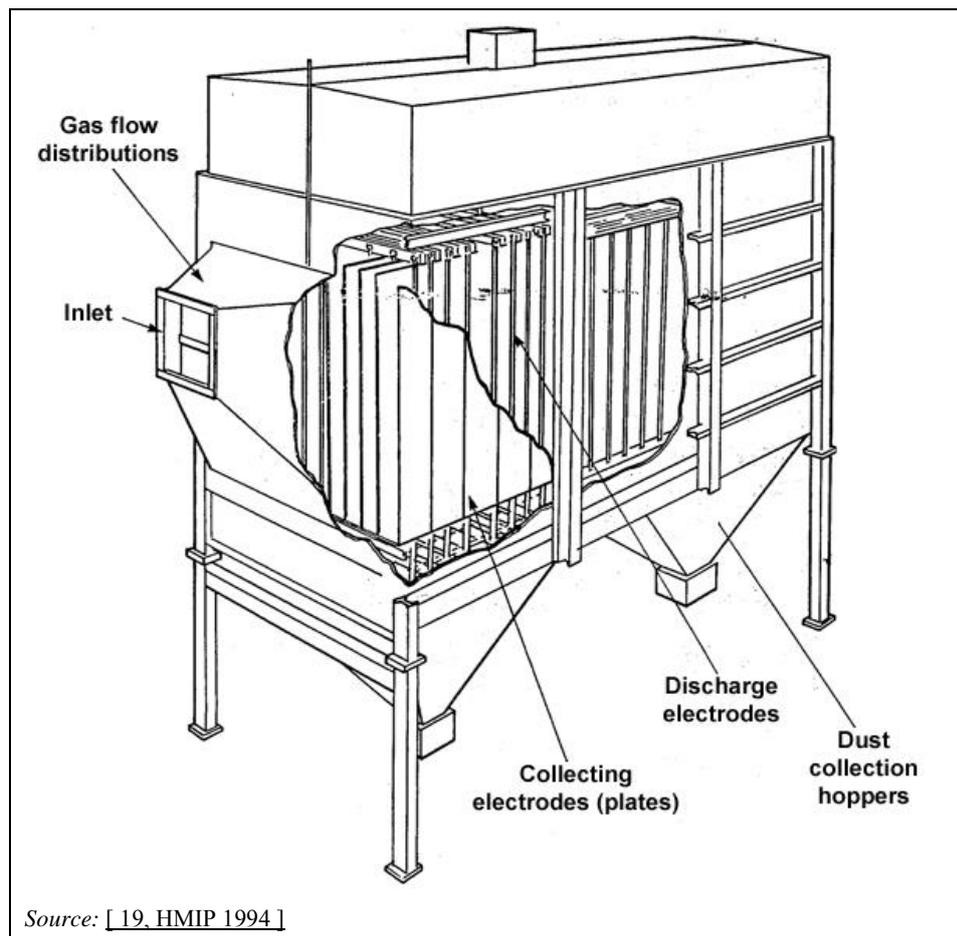
Figure 3.89: Wire plate ESP
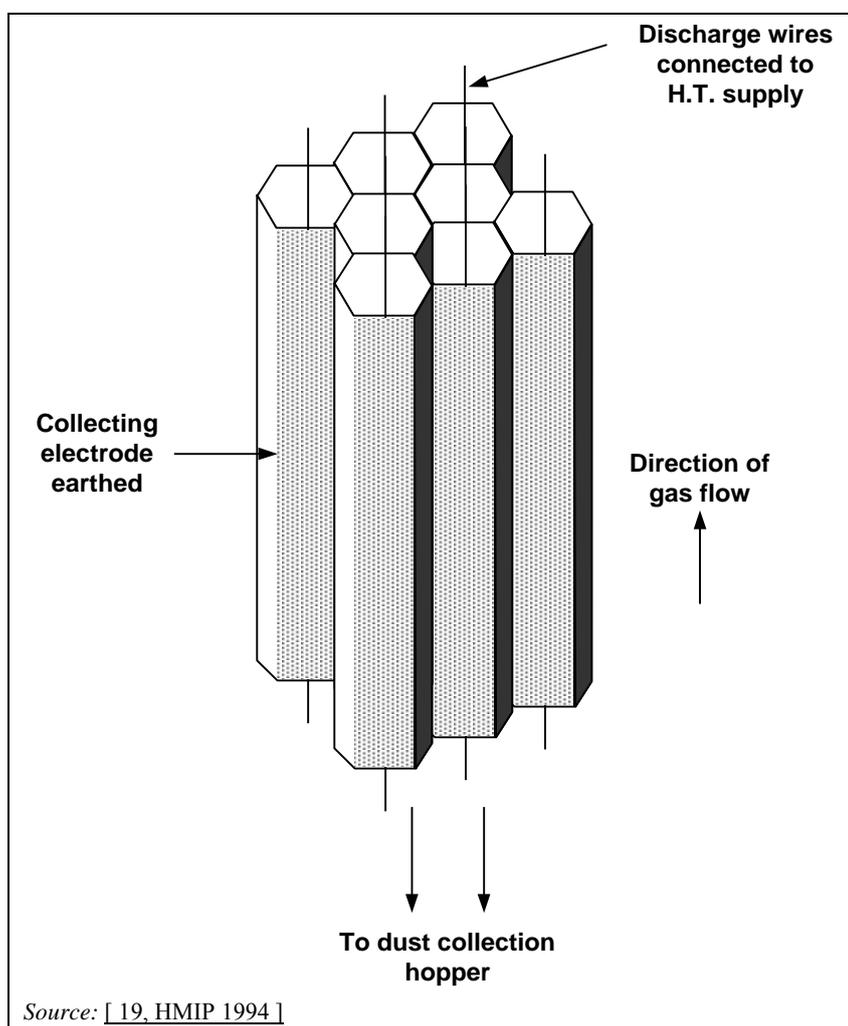
Figure 3.90: Dry wire pipe ESP

In dry ESPs, the collectors are knocked or rapped by various mechanical means to dislodge the particulate matter, which slides downwards 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. 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 ESPs can be cleaned acoustically with sonic horns. In contrast to wire plate ESPs, wire pipe ESPs provide no sneakage paths around the collecting region, but field non-uniformities may allow some particles to avoid charging.

In wet ESPs, the collectors are either intermittently or continuously washed by a spray of water, and the collection hoppers are replaced with a drainage system. The wet effluent is collected and treated. Wet ESPs 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 ESPs. 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 ESPs, 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-stage and two-stage ESPs is illustrated in Figure 3.91.
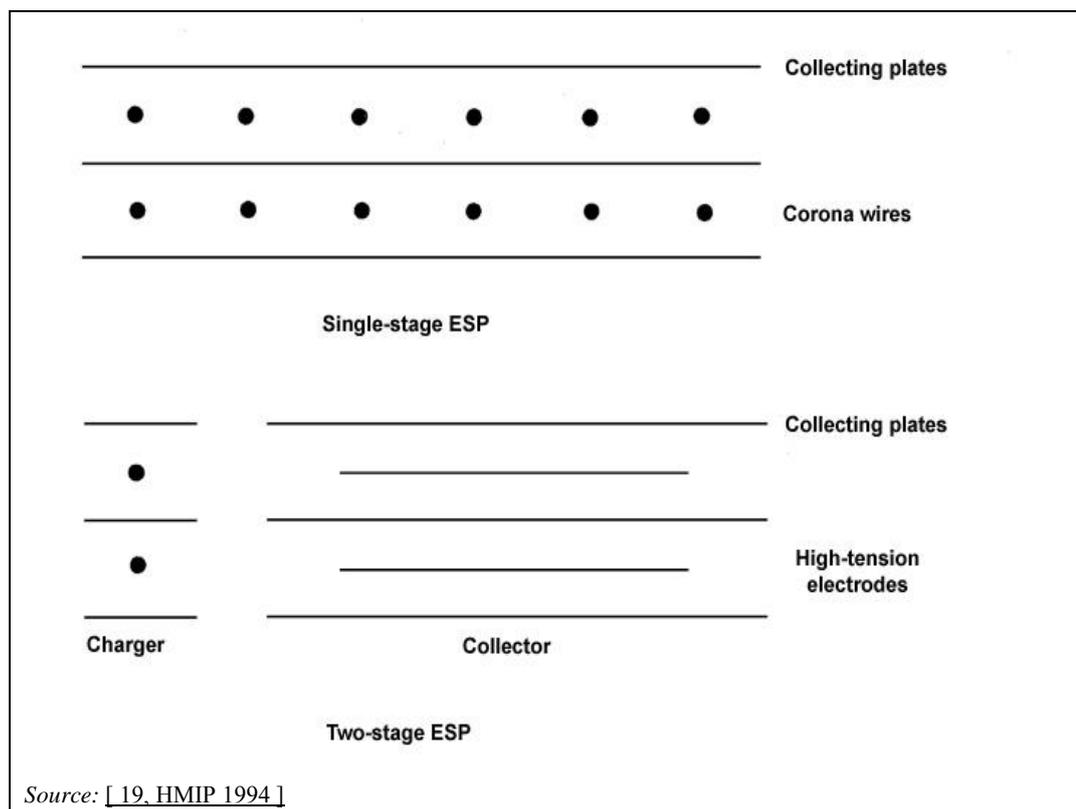
Figure 3.91: Single-stage and two-stage ESPs

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. A higher SCA equates to better removal efficiencies but also requires larger collectors. SCA are normally in the range of 40–160 s/m.

Systems with high risks, such as of explosion and fire, must be equipped with safety devices, e.g. explosion hatches or sprinkler systems.

Achieved environmental benefits
Abatement efficiencies and emission levels associated with electrostatic precipitators are given in Table 3.231.

Table 3.231: Abatement efficiencies and emission levels associated with electrostatic precipitators

Pollutant	Abatement efficiency (%)		Comments
	Dry ESP	**Wet ESP**	
Dust (PM size not identified)	NI	99.0–99.2 ([1])	—
Dust, aerosols	NI	97–99 ([1, 2])	Remaining emissions of 5–20 mg/Nm^3 ([3])
PM$_1$	> 97 ([2])	NI	
PM$_2$	> 98 ([2])	NI	
PM$_5$	> 99.9 ([2])	NI	
PM$_5$	> 99.9 ([3])	NI	—
PM$_{2.5}$	NI	97–99.2 ([1])	—
PM$_2$	> 98 ([3])	NI	—
PM$_1$	> 97 ([3])	NI	—
Parameter	Emission level ([4]) (mg/Nm^3)		Comments
	Dry ESP	**Wet ESP**	
Dust, aerosols	5–20 ([2])	NI	—

([1]) [62, US EPA 2003].
([2]) [176, Schenk et al. 2009].
([3]) [111, COM 2006] and [176, Schenk et al. 2009]; Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages.
([4]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].

NB: NI = no information provided.

Cross-media effects
Consumables associated with electrostatic precipitators are given in Table 3.232.

Table 3.232: Consumables associated with electrostatic precipitators

Consumable	Amount	Comments
SO$_3$ (if injected to reduce particle resistivity)	NI	—
NH$_3$ (if injected to reduce particle resistivity)	NI	—
Water (for wet ESP)	NI	—
Energy (kWh/1 000 Nm^3)	0.5–2 ([1])	—
	0.2–1 ([2])	Wet and dry ESP
DC voltage at the electrodes (kV)	20–100	—
Pressure drop (kPa)	0.05–0.3 ([1, 2])	Single-stage ESP
	0.5	Two-stage ESP

([1]) [9, BASF 1999].
([2]) [11, InfoMil 1999].
NB: NI = no information provided.

With dry ESPs, the separated dust is emitted as a residue; with wet ESPs, the separated dust merges with the rinsing water, which is treated as waste water. Wet ESPs require sufficient water to quench the waste gas to saturation, in addition to the water required for washing the plates. This continuous load is likely to be much higher than the wash water load [227, CWW TWG 2009].

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 should be disposed of accordingly.

Operational data
The size of the ESP is the main factor in determining the collection efficiency. Other parameters that affect the collection efficiency are:

- particle resistivity;
- composition of particles and gas stream;
- particle temperature and gas temperature;
- particle size and size distribution.

Particle resistivity can be reduced by injecting one or more of the following upstream of the precipitator:

- sulphur trioxide (SO_3),
- ammonia (NH_3),
- water.

However, by adding new reagents or water, the particles might no longer be reusable.

Design, construction and maintenance: [176, Schenk et al. 2009]
Typical design specifications are as follows:

- material of choice: steel;
- dimensioning basis (for dry ESP): gas flow, gas speed in filter (0.6–1 m/s);
- capacity ($m^3/1\ 000\ Nm^3$/h): 1.4–2.8.

Because of the electrodes being tapped, the removed dust can be collected in the dust funnel. However, when too many plates are being cleaned at the same time, the remaining emissions will be temporarily higher. It is thus beneficial to limit the amount of electrodes being tapped simultaneously. The plates should be tapped frequently in order to prevent the layer of fly ash from becoming too thick and thus decreasing the abatement efficiency. However, when the plates are tapped too often, the fly ash layer does not become thick enough and breaks off into pieces and is sucked away with the gas stream. The configuration of the plates is important in this regard, with low gas speed zones and the correct height/width ratio of the plates being essential for proper efficiency.

Monitoring [19, HMIP 1994]
The mass emission needed 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 a meter based, for example, on UV/visible opacity, beta rays or particle impingement.

Meters based on UV/opacity and beta rays should be calibrated periodically based on isokinetic sampling [227, CWW TWG 2009].

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.

ESPs 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.

Applicability
ESPs are applied to remove particulate matter down to $PM_{2.5}$ and smaller, and hazardous air pollutants, such as most metals.

Application areas in the industry are given in Table 3.233.

Table 3.233: Application of electrostatic precipitators

Sector	ESP type
Boilers	Dry wire plate
Chemical manufacturing (e.g. sulphuric acid)	Dry and wet wire plate, dry and wet wire pipe
Refineries, cement manufacturing, ferroalloy production, pulp and paper	Dry wire plate
Incineration	Dry wire plate, dry and wet wire pipe
Textile industry, pulp and paper industry, metallurgical industry (including coke ovens and hazardous waste incinerators)	Dry and wet wire pipe
Source: [59, US EPA 2003] [60, US EPA 2003] [61, US EPA 2003] [62, US EPA 2003].	

The applicability of dry ESPs to treat waste gases from units that combust liquid fuel can be limited due to a number of factors, including:

- very low particle resistivity;
- the type of particles (e.g. high cenosphere content);
- unfavourable flue-gas composition.

Wet ESPs are used in situations for which dry ESPs are not suited, such as:

- removal of particulates which are wet and sticky;
- treatment of flammable/explosive mixtures;
- control of aerosols, fumes and acid mists.

The single-stage ESP is used in large complex flue-gas treatment systems, e.g. in power stations (see the LCP BREF [111, COM 2006]) and waste incinerators (see the WI BREF [108, COM 2006]) 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. A single-stage ESP 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 given in Table 3.234.

Table 3.234: Application limits and restrictions associated with electrostatic precipitators

Issue	Limits/restrictions
Typical waste gas flow (Nm^3/h)	1 800–180 000 (dry wire pipe) ([1, 2])
	360 000–2 000 000 (dry wire plate) ([1])
	360 000–1 800 000 (dry wire plate) ([3])
	1 800–180 000 (wet wire pipe) ([1, 4])
	180 000–900 000 (wet wire plate) ([1, 5])
Temperature (°C)	Up to 700 (dry ESP) ([1, 2, 3])
	80–90 (wet ESP) ([1, 4, 5])
Pressure (mbar)	Atmospheric
Pressure drop (mbar)	0.5–3 ([1]) (dry ESP)
	Some pressure drop ([1]) (wet ESP)
Typical dust content (g/Nm^3)	1–10 (wire pipe) ([1, 2, 4])
	2–110 (wire plate) ([1, 3, 5])
Resistivity (Ω×cm)	5×10^3–10^{10} ([2, 3]) (dry ESP)
	5×10^3–10^{13} ([6]) (dry ESP)
Particulate size	PM$_{>1.0}$ (dry ESP)

([1]) [176, Schenk et al. 2009].
([2]) [59, US EPA 2003].
([3]) [60, US EPA 2003].
([4]) [61, US EPA 2003].
([5]) [62, US EPA 2003].
([6]) [227, CWW TWG 2009].

Advantages and disadvantages are given in Table 3.235.

Table 3.235: Advantages and disadvantages associated with electrostatic precipitators

Advantages	Disadvantages
• High abatement efficiency (> 97 %) even for small particles (efficiency can be increased by adding fields or zones) • Low-pressure drop, hence energy requirement tends to be low (in some applications, an induced or forced draft fan is needed to overcome system pressure drop) • Suitable for a wide range of temperatures, pressures and gas flows • Dust can be removed dry, making reuse possible (for dry ESP) • Partial removal of acid fumes (for wet ESP) • Wet ESPs can abate sticky particles, mists and highly resistive or explosive dusts • At a voltage of > 50 kV, abatement efficiency is independent of the residence time, enabling more compact construction (for wet ESP)	• Less suited for processes with varying gas streams, temperatures or dust concentrations. This, however, can be compensated for by automatic adjustments. Varying operational conditions are no problem, if the installation is designed for the worst case situation. • Re-entrainment can be a problem due to high gas velocities, poor rapping or poor gas flow • Sensitive to maintenance and settings • Relatively large space required • Highly qualified personnel is required • Special precautions to protect personnel from the high voltage • Explosion risk with dry ESPs • The abatement capacity depends on the resistivity of dust particles (with dry ESPs) • Dry ESPs not recommended for the removal of sticky or moist particles • Corrosion near the top of the wires because of air leakage and acid condensation, which is also an issue with wet ESPs • Wet ESPs are relatively expensive

Economics

Economics associated with ESPs are given in Table 3.236.

Table 3.236: Economics associated with electrostatic precipitators

Type of costs	Costs			
	Dry ESP	**Comments**	**Wet ESP**	**Comments**
Investment costs (k EUR/1 000 Nm³/h)	50–500 ([1, 2])	–	Typically 30 % higher than for dry ESP	–
Operating costs (EUR/1 000 Nm³/h)	0.05–0.1	For systems of > 50 000 Nm³/h	0.05–0.1	For systems of > 50 000 Nm³/h
Labour (h/d)	~ 0.25	Maintenance of electrodes	~ 0.25	Maintenance of electrodes
Waste treatment (EUR/t)	~ 75	Non-hazardous waste	~ 75	Non-hazardous waste
	150–250	Hazardous waste	150–250	Hazardous waste
Cost-determining parameters	Gas flow, waste gas temperature, dust concentration, abatement efficiency			
Benefits	None, unless dust materials is recovered and reused/recycled			

([1]) [227, CWW TWG 2009].
([2]) A revamp project executed in France (completed by the end of 2008) which consists of adding an ESP on the stack of a boiler burning heavy fuel resulted in total construction costs of EUR 27.4 million for a flow rate of 311 kNm³/h which leads to a cost of 88 k EUR/kNm³ [189, de Borman 2010].
NB: NI = no information provided.
Source: [176, Schenk et al. 2009].

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.

Driving force for implementation
Reduction of particulate matter emissions as well as material recovery are the main driving forces for implementation of the technique.

Example plants
Dry ESPs are reported to be used in the chemical industry sector as well as in other sectors such as large combustion plants, refineries, and waste incineration.

Wet ESPs are reported to be used in small-scale waste gas cleaning systems in the metal industry and the chemical industry where dry ESPs do not suffice when handling wet and sticky matter, flammable and explosive mixes and material with a high resistance.

Reference literature
[9, BASF 1999] [11, InfoMil 1999] [19, HMIP 1994] [59, US EPA 2003] [60, US EPA 2003] [61, US EPA 2003] [62, US EPA 2003] [108, COM 2006] [111, COM 2006] [176, Schenk et al. 2009] [189, de Borman 2010] [227, CWW TWG 2009]

3.5.1.4.5 Wet dust scrubber

Description
Wet dust scrubbing is a variation of wet gas scrubbing (see Section 3.5.1.2.4), using the same or equivalent techniques to abate or recover particulate matter in addition to gaseous compounds.

Wet dust scrubbing entails separating the dust by intensively mixing the incoming gas with water, usually combined with a removal of the coarse particles through the use of centrifugal force. In order to achieve this, the gas is inserted tangentially (at an angle from the side). The removed solid dust is collected at the bottom of the dust scrubber. Aside from the dust, inorganic chemicals such as SO_2, NH_3, NH_4Cl, VOCs and heavy metals that may be attached to the dust are removed. The major goal for which the scrubber is applied is the removal of the dust.

The different scrubbers operated are mainly the following:

- **Fibrous packing scrubbers** which are mainly suitable for gaseous contaminants. For particulate matter, they are restricted to collecting fine and/or soluble particulate matter, aerosols and mists. Insoluble and/or coarse particulates clog the fibre bed (see Section 3.5.1.2.4).
- **Moving-bed scrubbers** (see Section 3.5.1.2.4).
- **Plate scrubbers** the primary application being for particle removal (See Section 3.5.1.2.4).
- **Spray towers** in which the washing liquid is sprayed or scattered by a fast-spinning nebuliser disc or rotating sprays, creating a large contact surface for the drops and the inlet gas. There are variations of the spraying tower that do not have a spinning turbine. The gas is inserted tangentially (at an angle from the side) into the dust removal chamber. The centrifugal forces and the rotating nebulas drag the dust particles to the chamber wall, making high removal efficiency possible. The primary application of spray towers is small particle removal ($PM_{< 10}$). 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 matter (see Section 3.5.1.2.4). A schematic of a spray tower scrubber is shown in Figure 3.92.
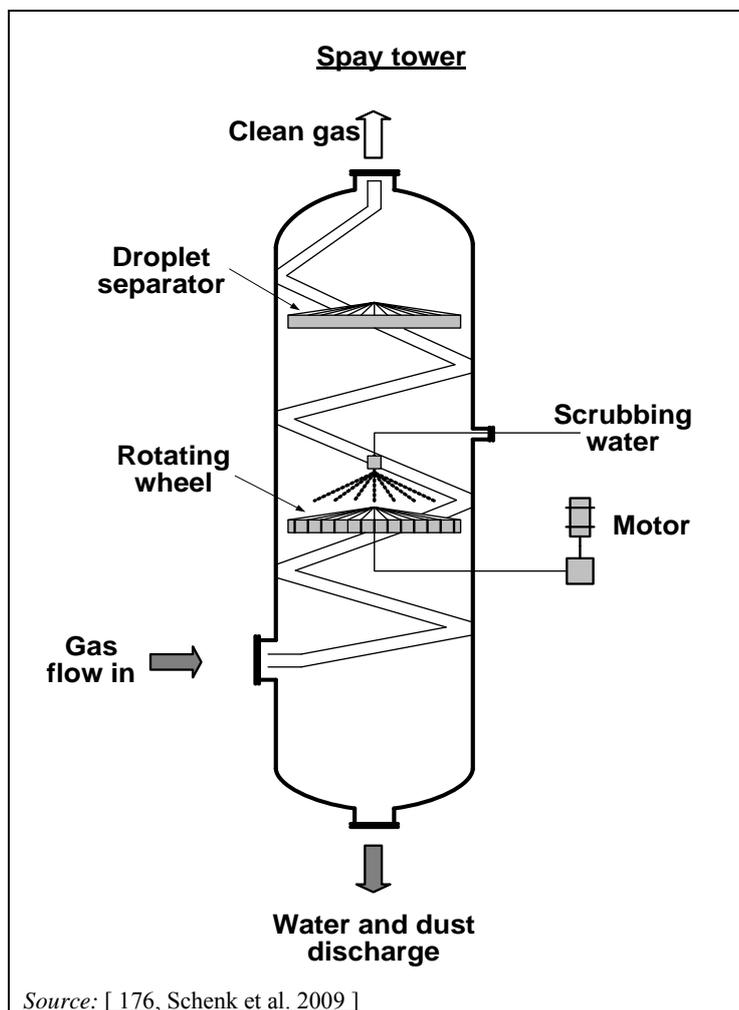
Figure 3.92: Spray tower

- **Impingement entrainment scrubbers** which 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. A schematic of an impingement entrainment scrubber is given in Figure 3.93.
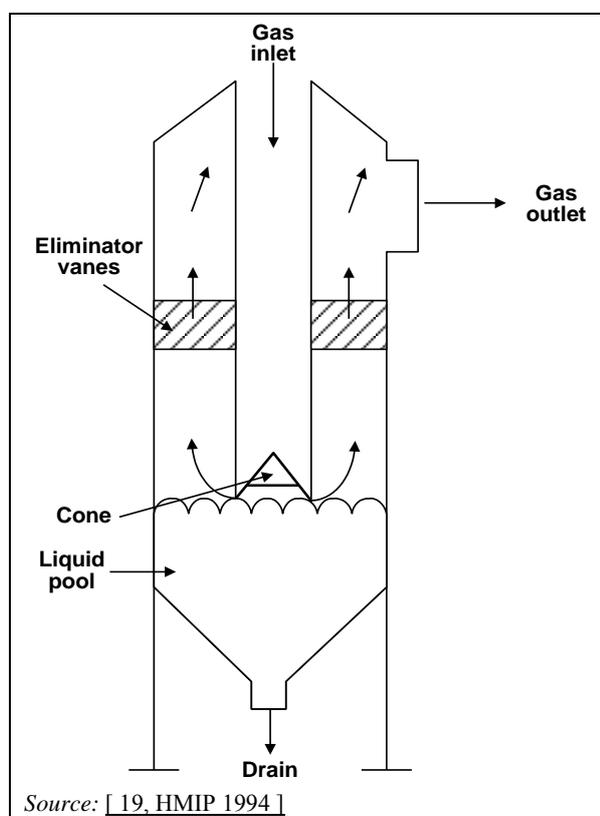
Figure 3.93: Impingement entrainment scrubber

- **Venturi scrubbers**, the characteristic feature being the constriction of the duct – Venturi throat – causing an increase in gas velocity. Liquid is introduced into 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 for particles down to submicron size. They can also be used to remove trace gases, particularly reactive slurries. An example is given in Figure 3.94.

  A problem encountered with this technique 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 and chemical attacks.

  The 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.

  A variant of the Venturi scrubber is the vane-cage scrubber containing internal static blades creating a mist [176, Schenk et al. 2009].
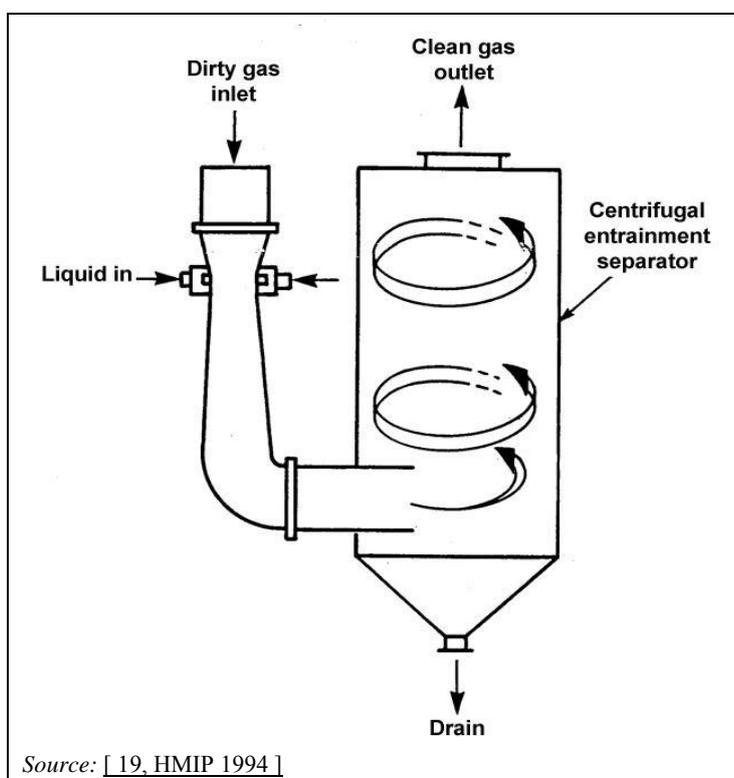
Figure 3.94: Venturi scrubber

Achieved environmental benefits
The performance of wet dust scrubbing techniques is highly dependent on the size of the particulate matter and the aerosols to be collected. The abatement efficiencies are given in Table 3.237.

Cross-media effects
The consumables are given in Table 3.237.

With a wet dust removal technique, pollution is transferred into the washing medium (water) and waste water treatment is therefore needed.

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.

Table 3.237: Abatement efficiency, consumables and costs of the wet dust scrubber variants

Pollutant ([1])	Abatement efficiency (%)					
	Fibrous packing	Moving-bed	Plate	Spray tower	Impingement entrainment	Venturi
Dust (PM size not identified)	70–> 99 ([2])	NI	50–99 ([3])	70–> 99 ([4, 5, 6])	80–99 ([7])	70–> 99 ([8, 9])
PM_{10}	NI	NI	NI	70–> 99 ([5, 6])	NI	70–99 ([10])
$PM_{0.3–0.5}$	NI	NI	NI	NI	NI	< 50 ([5, 11])
VOCs	70–> 99 (mists) ([2])	NI	NI	50–95 ([4])	NI	NI
SO_2	NI	NI	80–> 99 ([3])	80–> 99 ([4])	NI	NI
HCl	NI	NI	NI	NI	NI	50–90 ([5])
HF	NI	NI	NI	NI	NI	50–90 ([5])
NH_3	NI	NI	NI	94–99 ([12])	NI	94–99 ([12])
Consumable	**Amount of consumables**					
Scrubbing water (l/Nm^3)	NI	NI	NI	> 3 ([4])	NI	0.5–5 ([13])
Chemical additives to improve precipitation	NI					
Energy (kWh/1 000 Nm^3/h)	NI	NI	NI	0.4–2.7 ([13]) depending on design	1–2 ([13])	0.5–7 ([13])
Pressure drop (kPa)	NI	NI	NI	Low	1.5–2.8 ([13])	2.5–20 ([9, 13])
Type of costs	**Costs**					
Investment costs (per 1 000 Nm^3/h)	USD 600–1 800 (EUR 460–1 380) ([2])	NI	USD 1 300–7 000 (EUR 1 390–7 480) ([3])	EUR 5 000–25 000 ([14, 15])	USD 2 800–10 000 (EUR 2 140–7 650) ([7])	EUR 5 000–7 000 ([14])
Operating costs (per 1 000 Nm^3/h)	USD 1 000–21 100 (EUR 770–16 100) ([2])	NI	USD 1 500–41 100 (EUR 1 600–43 900) ([3])	EUR 1 000–30 000 ([14])	USD 2 200–42 000 (EUR 1 680–32 100) ([7])	EUR 2 000–50 000 ([14]) ([16])
Labour (h/month)	~ 4					
Treatment of residues (EUR/t)	NI	NI	NI	EUR 100–250 ([14])	NI	NI
Cost-effectiveness (per t of pollutant abated)	USD 40–710 (EUR 31–540) ([2])	NI	USD 51–1 300 (EUR 54–1 390) ([3])	USD 28–940 (EUR 30–1 000) ([4])	USD 88–1 400 (EUR 67–1 070) ([7])	USD 84–2 300 (EUR 90–2 460) ([8])

Pollutant ([1])	Abatement efficiency (%)					
	Fibrous packing	Moving-bed	Plate	Spray tower	Impingement entrainment	Venturi
Cost-determining parameters	Scale of scrubber and potentially special treatment of gas stream					
Benefits	None					

([1]) PM is the pollutant targeted by the technique, other pollutants are abated as a positive side effect.
([2]) Cost data for 1995 [45, US EPA 2003]. Average currency conversion rate for 1995: EUR/USD = 1.307.
([3]) Cost data for 2002 [46, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([4]) Cost data for 2002 [49, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([5]) [176, Schenk et al. 2009]; Remaining emissions may be < 10 mg/Nm^3; efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages.
([6]) Including particles down to 1–2 μm [176, Schenk et al. 2009].
([7]) Cost data for 1995 [47, US EPA 2003]. Average currency conversion rate for 1995: EUR/USD = 1.307.
([8]) Cost data for 2002 [50, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([9]) [11, InfoMil 1999].
([10]) Depending on the particle sizes [176, Schenk et al. 2009].
([11]) The efficiency is particularly low with pollutants that are not easily humidified [176, Schenk et al. 2009].
([12]) [71, US EPA 1995] Fertiliser industry, phosphoric acid as a scrubbing liquor.
([13]) [250, Ullmann's 2011].
([14]) [176, Schenk et al. 2009].
([15]) For capacities of > 10 000 Nm^3/h, an upscaling to the power of 0.3 applies (i.e. additional costs > price$^{0.3}$ for extra capacities beyond 10 000 Nm^3/h) [176, Schenk et al. 2009].
([16]) EUR (2 500 + 100 × (flow/1 000)).

NB: NI = no information provided.

Scrubbing devices are sources of noise, which needs to be abated accordingly, e.g. by enclosing the equipment.

Operational data

Design and maintenance

The liquid to gas ratio of a dust scrubber is the ratio between the gas flow and the scrubber liquid flow. For the proper dimensioning and evaluation of the performance of a dust scrubber, it is important to know how much liquid per Nm^3 is necessary to achieve the targeted emission level. The performance depends to a great extent on the degree of pollution of the dust scrubber. Regular inspection, maintenance and cleaning are all necessary for a proper performance.

The **Venturi scrubber** itself has a small volume capacity. The total size of the installation is primarily determined by the demister, which may be several times the size of the scrubber. A liquid to gas (L/G) ratio of 1–5 m^3 per 1 000 Nm^3/h can be used as a guideline. The Venturi is often constructed of erosion-proof and corrosion-proof material in order to significantly lengthen its lifespan. The drip catcher should be checked for pollution regularly. In general, the Venturi scrubber requires very little maintenance.

Monitoring [11, InfoMil 1999]

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, for example, on UV/visible opacity, beta rays or particle impingement. Meters based on UV/opacity and beta rays should be calibrated periodically based on isokinetic sampling. The pressure drop across the scrubber, the liquid/reagent flow rate and the feed pressure need to be routinely monitored. The liquid/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 easy access to the scrubbers.

Applicability

Applicability and application limits of wet dust scrubber systems are given in Table 3.238.

Table 3.238: Applicability, application limits and restrictions associated with different wet dust scrubbers

Issue	Fibrous packing	Moving-bed	Plate	Spray towers	Impingement entrainment	Venturi
Issue	Collects fine and/or soluble PM. Used as a mist eliminator to collect liquid aerosols, inorganics and VOCs. Controls aerosol emissions from chemicals, plastics, asphalt, sulphuric acid, and surface coating industry. Only limited acceptance for dust collection ([1])	NI	Collection of PM_{10}, $PM_{2.5}$, PM_{HAP}, inorganic fumes, vapours, gases, VOC ([2])	Collection of PM_{10}, $PM_{2.5}$, PM_{HAP}, inorganic fumes, vapours, gases, VOCs. Often used as part of flue-gas desulphurisation. Only limited usage for fine PM ([3])	Collection of PM_{10}, $PM_{2.5}$, down to PM_2. Used in pharmaceutical processing and packaging, manufacturing of chemicals, rubber, plastics, ceramics, and fertilisers. Processes controlled include drying, cooking, crushing and grinding operations, spraying, ventilation, material handling ([4])	Collection of $\leq PM_{10}$, $\leq PM_{2.5}$, down to submicron sizes. Controls PM emissions from utility, industrial, commercial and institutional boilers fired with coal, oil, wood and liquid waste. Controls emission sources in chemical and related industries. Typically applied where high collection efficiencies for fine PM are required ([5])
Gas flow (Nm^3/h)	1 800–170 000 ([1])	NI	1 700–130 000 ([2])	2 500–170 000 ([3])	1 700–90 000 ([4])	720–100 000 ([5])
Temperature (°C)	< 60 ([1])	NI	4–370 (PM) ([2])	4–370 (PM) ([3])	Up to 150 ([4])	4–370 ([5, 6])
Temperature (°C)	NI	NI	4–38 (gases) ([2])	4–38 (gases) ([3])	Up to 150 ([4])	4–370 ([5, 6])
Pollutant loading (PM) (g/Nm^3)	0.2–11 ([1])	NI	No limits	No limits	Up to 23 ([4])	1–115 ([5])
Pressure	Atmospheric ([7])					
Pressure drop (mbar)	20–50 ([7])					25–200 ([7])

([1]) [45, US EPA 2003].
([2]) [46, US EPA 2003].
([3]) [49, US EPA 2003].
([4]) [47, US EPA 2003].
([5]) [50, US EPA 2003].
([6]) The Venturi scrubber is also used as a cooler to quench hot gases (up to 1 000 °C) [176, Schenk et al. 2009].
([7]) [176, Schenk et al. 2009].
NB: NI = no information provided.

Advantages and disadvantages are given in Table 3.239.

Table 3.239: Advantages and disadvantages associated with wet dust scrubbers

Advantages	Disadvantages
General • Can handle gas streams which contain flammable and explosive chemicals with low risk • Provides cooling for hot gases • Corrosive gases can be neutralised • Simultaneous removal of dust and inorganic compounds	General • Significant water usage and generation of waste water • Relatively large space required • Waste (or by-product if reused or recycled) 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 (can be solved with proper material selection) • Not really suitable for collecting 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 (can be solved with proper material selection)
Spray towers • Ability to collect even small PM as well as gases • Relatively free from plugging • Relatively small space requirements • Relatively low pressure drop • Insensitive to fluctuating gas flow	Spray towers • Relatively low mass transfer efficiencies • With FRP construction, sensitive to temperature • Relatively high energy consumption • Relatively large investment costs
Impingement entrainment scrubbers • Can handle mists • Relatively low water recirculation rate • Collection efficiency can vary	Impingement entrainment scrubbers • High potential for corrosion problems (can be solved with proper material selection)
Venturi scrubbers • Can handle mists • Relatively low maintenance • High removal efficiency rate • Simple and compact in design and easy to install • Insensitive to fluctuating gas flow • Collection efficiency can be varied • Also removes reactive gaseous contaminants • Free from clogging	Venturi scrubbers • High potential for corrosion problems (can be solved with proper material selection) • Relatively high pressure drop, and hence high energy requirement for some Venturi scrubbers • Noise may be a problem since gas velocity at the Venturi throat is high • Limited to the control of PM and gases with high solubility in water

Economics

The cost ranges for wet dust scrubbers are given in Table 3.237. 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.

Driving force for implementation
Abatement of particulate matter emissions as well as abatement of inorganic chemicals (such as SO_2, NH_3, NH_4Cl, VOCs) and heavy metals that may be attached to the dust are the main driving forces for implementation of the technique.

Example plants
The technique is reported to be widely used in the chemical industry sector as well as in other sectors such as in asphalt production, the metal industry, waste incineration, the potato processing industry (for the removal of amylum), the pulp and paper industry, the glass industry, refineries (used on catalytic crackers), and foundries.

Reference literature
[11, InfoMil 1999] [19, HMIP 1994] [45, US EPA 2003] [46, US EPA 2003] [47, US EPA 2003] [49, US EPA 2003] [50, US EPA 2003] [71, US EPA 1995] [176, Schenk et al. 2009] [250, Ullmann's 2011]

3.5.1.4.6   Fabric filter

Description
In a fabric filter (also called a bag filter), waste gas is passed through a tightly woven or felted fabric, causing particulate matter to be collected on the fabric by use of a sieve or other mechanisms (see Figure 3.95). 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.


Source: [176, Schenk et al. 2009]
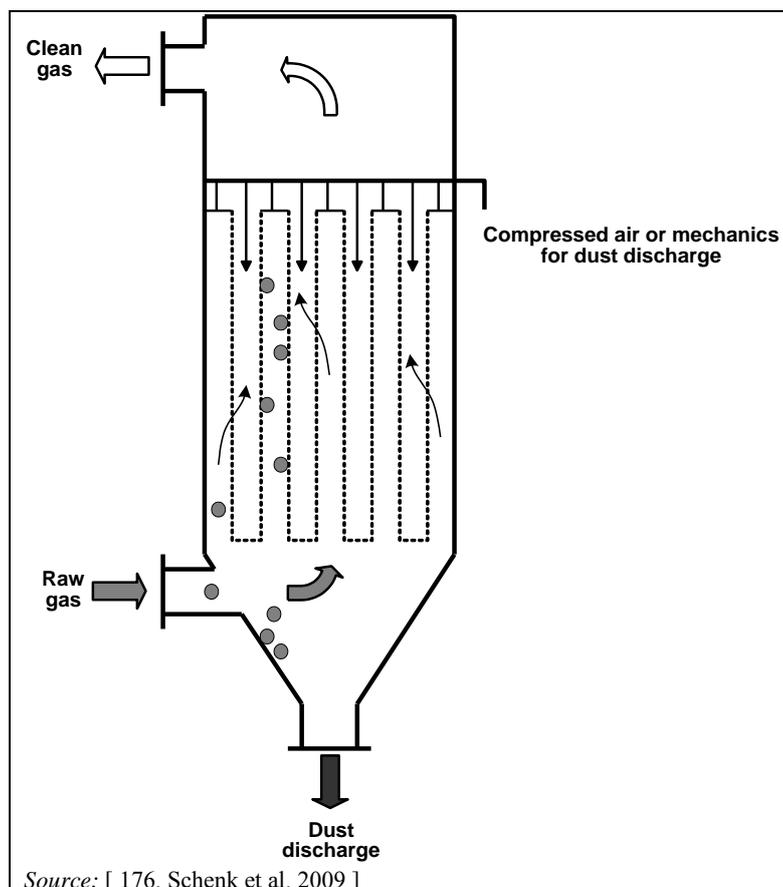
Figure 3.95: Fabric filter

Operating conditions are important determinants in the choice of fabrics. Some commonly used fabrics are shown in Table 3.240.

Table 3.240: Commonly used fabrics

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
Acrylic copolymer	Good	Fair	110	120	130	No
m-Aramid	Good	Good	177	200	240	No
Polyphenylensulphide	Excellent	Excellent	190	190	232	No
Ethylene chlorotrifluoroethene	Excellent	Excellent	177	177	190	No
Polytetrafluoroethene (PTFE)	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	1 204	No

The 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 airflow 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 frequencies 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 as follows:

- **Reverse-air (or reverse-jet) cleaned fabric filter** which uses a gentler but sometimes less effective cleaning mechanism than mechanical shaking. Typically, the bags are open on the bottom, closed on top, and the dust is captured on the inside or the outside of the bags. To clean the filter, it is taken offline and clean air is forced through it in the opposite direction, and the dust cake falls off into the hopper. The typical cleaning cycle lasts < 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** which uses 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, and the particles are 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** which uses a relatively new method that can treat high dust loads, operate at a constant pressure drop and occupy less space than other fabric filter types. It can only operate as an external dust collection device. 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, and the particles are collected on the outside of the bags and drop into the hopper. Pulse-jet cleaning means the injection of a short burst (0.03–0.1 seconds) of highly 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 compounds, especially at temperatures below dew point. For appropriate filter fabrics see Table 3.240.

Other filters related/similar to fabric filters are the following:

- **The compact filter** which is also known as a cassette filter or an 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 partially cancelled out by the lower fabric load of this type of filter.
- **The 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. Additional information on this type of filter can be found in the Ceramic Manufacturing Industry (CER) BREF [117, COM 2007].

The gas temperature needs to be above the dew point of all the constituents because otherwise the filter fabric clogs and the filtration process stops. To prevent this, the baghouse might need to be insulated and possibly heated.

Systems with a high risk, such as of explosion and fire, should be equipped with safety facilities, e.g. explosion hatches or sprinkler systems. On the inlet side of the filter, there should be a relief valve 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 permitted.

Achieved environmental benefits
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 constant outlet devices rather than constant efficiency devices. Abatement efficiencies and emission levels associated with fabric filters are given in Table 3.241.

Table 3.241: Abatement efficiencies and emission levels associated with fabric filters

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm^3)
Dust (PM size not identified)	99–99.9 ([3])	2–10 ([3])
	99.95 ([4])	< 5 ([4])
Dioxins/furans ([5])	NI	0.1 ng/Nm^3 TEQ ([4])
([1]) Depending on the specific configuration, operational conditions and reagents. Values are based upon half-hourly averages [176, Schenk et al. 2009]. ([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009]. ([3]) [58, US EPA 2003]. ([4]) [176, Schenk et al. 2009]. ([5]) Dioxins/furans in the gas phase can be abated when activated carbon is injected into the waste gas upstream of the filter. NB: NI = no information provided.		

Cross-media effects

Consumables associated with fabric filters are given in Table 3.242.

Table 3.242: Consumables associated with fabric filters

Consumable	Amount	Comments
Filter fabric (m^2 per 1 000 Nm^3/h)	11–17	A/C ratio 1–1.5 m/min
Precoating material (optional)	NI	For sticky or static dust or as fabric protection
Compressed air (kPa)	300–700	Filter cleaning
Energy (kWh/1 000 Nm^3)	0.2–2	―
Pressure drop (kPa)	< 1.5	―
NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].		

The separated dust – possibly mixed with precoating 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 should be disposed of accordingly.

Operational data

Design and maintenance [176, Schenk et al. 2009]

The most important design parameters are as follows:

- Incoming gas flow.
- Working temperature and maximum temperature.
- Incoming gas composition.
- Fabric filter load (filter ratio). The fabric filter load is dependent on the type and nature of the cloth material, the dust load and the type and size of the particles. Examples are glass fibre: 60–120 m/h; and PTFE (Teflon): 80–100 m/h.
- The ease of cleaning and the design of the exterior, important for hygiene reasons in the food industry.

Monitoring [19, HMIP 1994]
Performance and maintenance have to be carefully monitored. 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, for example, on, 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 an alarm.

Applicability
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 (except mercury). In combination with injection systems (including adsorption – see Section 3.5.1.2.3, and dry lime/sodium bicarbonate injection and semi-dry lime injection – see Section 3.5.1.5.2) upstream of the baghouse, it can also be applied to remove specific gaseous contaminants.

Fabric filters are useful for collecting particulate matter with electrical resistivities either too low or too high for ESPs (see Section 3.5.1.4.4), hence they are suitable to collect fly ash from low-sulphur coal or fly ash which contains 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, ESPs or spray coolers may be used to reduce the load for the fabric filter, especially at high inlet concentrations.

Application limits and restrictions are given in Table 3.243.

Table 3.243: Application limits and restrictions associated with fabric filters

Issue	Limits/restrictions
Typical waste gas flow (Nm³/h)	300–1 800 000 ([1,2])
Temperature (°C)	See Table 3.240. Above the dew point of all condensables in the gas stream, otherwise the filter clogs. < 280, depending on the type of cloth ([2])
Pressure	Range -6.4–6.4 kPa around atmospheric pressure ([1])
Dust content (g/Nm³)	0.1–230 ([1,2]) 1–23 (typical) ([1])
Particle properties	Sticky dusts are difficult to remove from the filter media, hence they need to be avoided
A/C ratio ([3]) (m/min)	≤ 1 ([4]) (reverse-air filter) < 0.5 ([4]) (mechanical shaker filter) 1–1.5 (2.0) ([4,5]) (pulse-jet filter)
([1]) [58, US EPA 2003]. ([2]) [176, Schenk et al. 2009]. ([3]) Recommended to ensure proper operation (see above). ([4]) Personal communication. ([5]) Higher value for special arrangements.	

Advantages and disadvantages are given in Table 3.244.

Table 3.244: Advantages and disadvantages associated with fabric filters

Advantages	Disadvantages
• In general, fabric filters provide high abatement 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 reused in the preceding process or recycled • Residual emissions are virtually independent of the intake concentration • Relatively simple operation • Reliability	• Fabric filters are not suitable for wet or sticky dusts because of the risk of filter clogging • Heating the waste gas stream prevents condensation of fluid on the ceramic filters • Static electricity may hinder the cake from being removed from the fabric • Takes up a lot of space

Economics

The working life of filter material is about five years for fabric filters. Economics associated with fabric filters are given in Table 3.245.

Table 3.245: Economics associated with fabric filters

Type of costs	Costs		
	Fabric filter		
	Reverse-air	Mechanical shaker	Pulse-jet
Investment costs (per 1 000 Nm^3/h)	EUR 1 000–4 500 ([1])		
Filter material costs ([2]) (per 1 000 Nm^3/h)	EUR 660–920 ([1])		
Sonic horn costs ([2]) (per 1 000 Nm^3/h)	USD 300–400 (EUR 320–430) ([3, 5])	USD 300–400 (EUR 320–430) ([4, 5])	NI
Reverse-jet equipment costs ([2]) (per 1 000 Nm^3/h)	USD 600–1 200 (EUR 640–1 280) ([3, 5])	NI	NI
Operating costs (per 1 000 Nm^3/h)	EUR 200–1 500 ([1])		
Waste treatment costs (per t)	NI	NI	NI
Labour (h/week)	2 ([1])		
Cost-effectiveness (per tonne of pollutant)	USD 58–372 (EUR 62–397) ([3, 5])	USD 41–334 (EUR 44–357) ([4, 5])	USD 46–293 (EUR 49–313) ([5, 6])
Cost-determining parameters	Pressure drop, and potential costs for conveying dust		
Benefits	Savings in costs of raw materials when reuse/recycling is possible, for instance in the glass industry		

([1]) [176, Schenk et al. 2009].
([2]) On top of the investment costs.
([3]) Cost data for 2002 [58, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([4]) Cost data for 2002 [56, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
([5]) For pollutant loads of 9 g/Nm^3 and flow rates of between 1 700 000 Nm^3/h (minimum costs) and 3 500 Nm^3/h (maximum costs).
([6]) Cost data for 2002 [57, US EPA 2003]. Average currency conversion rate for 2002: EUR/USD = 0.9359.
NB: NI = no information provided.

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.

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.

Driving force for implementation
The driving forces for implementation include legal requirements and raw material savings.

Example plants
The technique is reported to be widely used in the chemical industry sector as well as in other sectors such as the food, drink and milk industries, the waste processing industry, the metal industry, waste incineration, large combustion plants, ceramics manufacturing and the glass industry.

Reference literature
[9, BASF 1999] [11, InfoMil 1999] [19, HMIP 1994] [56, US EPA 2003] [57, US EPA 2003] [58, US EPA 2003] [117, COM 2007] [154, Startin 2008] [176, Schenk et al. 2009]

3.5.1.4.7   Ceramic and metal filters

Description
Ceramic filters
In a ceramic filter (see Figure 3.96), the contaminated gas is led through the filtering material, in a process comparable to that of a fabric filter. The difference with a fabric filter is that the filtering material is ceramic. There are also designs where acidic compounds such as HCl, NO_X, SO_X and dioxins are removed. In such a case, the filtering material is fitted with catalysts and the injection of reagents may be necessary (see Section 3.5.1.5.2).

The filtering material of a ceramic filter can be applied in many different forms. It is possible to convert the ceramic material into cloth, fibre felt, fibre elements, sinter elements or filter candles. Table 3.246 below gives an overview of the different applications.

Table 3.246: Overview of different filtering materials in ceramic filters

Filter medium	Filter cloth	Fibre felt	Fibre element	Sinter element
Design	Bag with supporting basket	Bag with supporting materials	Pipe, self-carrying	Pipe, candle, self-carrying
Surface weights (g/m^2)	1 000–2 000	2 500–3 000	2 000–4 500	12 500–22 800
Mechanical qualities	Flexible, not very grating-proof	Flexible, not very grating-proof	Semi-flexible, somewhat grating-proof	Stiff, grating-proof
Air transparency	High	Average	Average	Low
Source: [176, Schenk et al. 2009].				

Source: [176, Schenk et al. 2009]
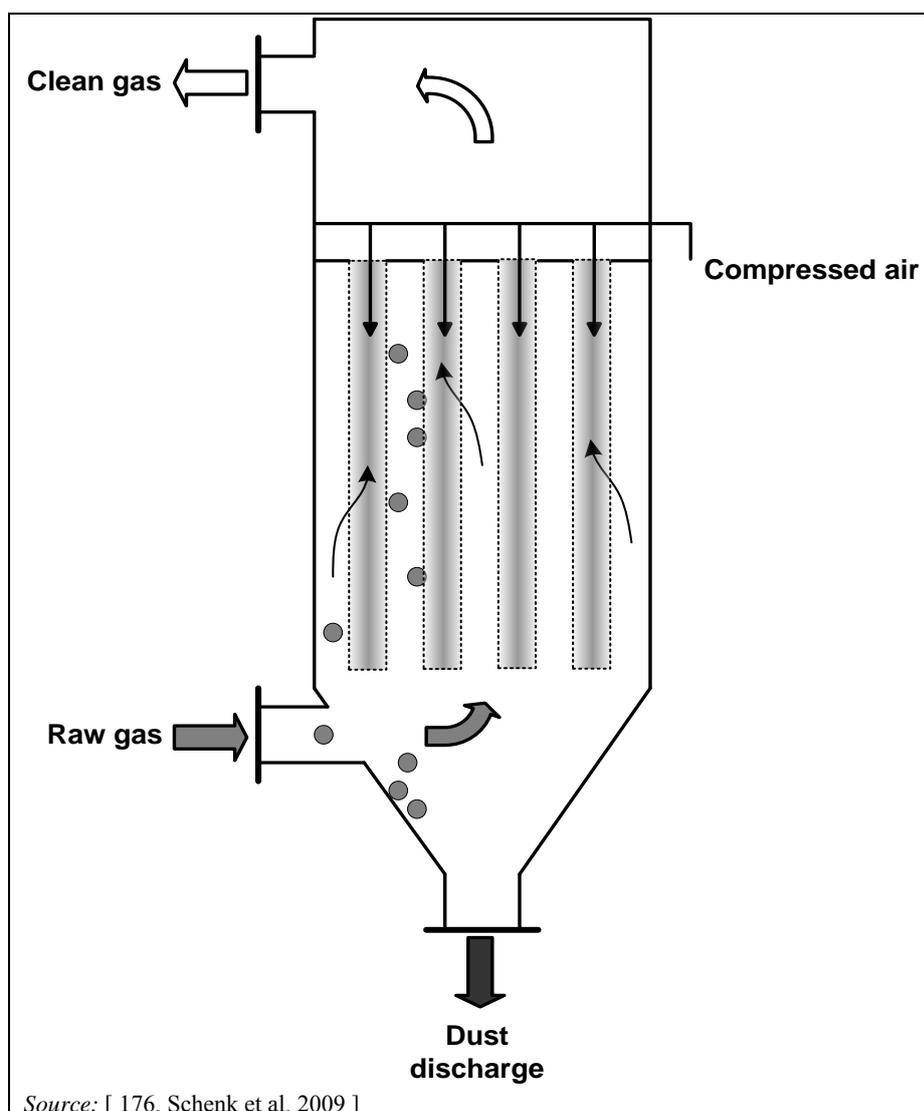
Figure 3.96: Ceramic filter

Metal filters
In metal filters, surface filtration is carried out by sintered porous metal filter elements. Metal filters can withstand temperatures of up to 1 000 °C and pressure in excess of 69 bar.

Sintered metal filter media are typically applied in automatically regenerated filter systems, installed in processes where regular, conventional synthetic (textile) or glass fibre filter media are no longer suitable due to the excessively high operating temperature (> 300 °C). The elements can be easily reverse- (or pulse-) jet cleaned by means of compressed air, nitrogen or clean process gas, depending on the composition.

Sintered metal filter media supersede ceramic filter elements when it comes to mechanical strength and resistance against thermal shock. Ceramic filter media are very sensitive to temperature fluctuations.

Besides the high temperature resistance of the porous sintered metal filter elements, there is a wide range of materials available that can be selected for each specific process. The most commonly used materials are SS304, SS316, Inconel, Hastelloy and Fecralloy, dependent on the required chemical resistance.

Due to the high porosity, the differential pressure drop is typically very low (< < 10 mbar). Emission levels below < 1 mg/Nm^3 can be achieved.

Sintered metal filter elements are relatively expensive compared to other conventional filter media. However, due to their specific excellent properties, sintered porous metal filter elements are typically applied in heavy-duty, industrial applications, e.g. for emission reduction (mainly catalyst fines) at petrochemical plants as well as for solids removal from bottom products like Fluidised Catalytic Cracking Units and Coker Units. The mechanical and thermal strength of sintered porous metal media makes them very suitable for high-temperature processes, where lifetimes of > 4 years without unplanned stops need to be guaranteed [239, Hage 2009].

Achieved environmental benefits
Abatement efficiencies and emission levels associated with ceramic and metal filters are given in Table 3.247.

Table 3.247: Abatement efficiencies and emission levels associated with ceramic and metal filters

Pollutant	Ceramic filters		Metal filters	
	Abatement efficiency[1] (%)	Emission level [2] (mg/Nm^3)	Abatement efficiency (%)	Emission level (mg/Nm^3)
Dust (PM size not identified)	99–99.99 [3]	< 1 [4]–< 2 [3]	> 99.99 [5]	NI
Dioxins/furans [6]	99 [3]	NI	NI	NI
HCl	95 [3]	NI	NI	NI
SO$_2$	80 [3]	NI	NI	NI
NO$_X$	95 [3]	< 200 [3]	NI	NI

[1] Depending on the specific configuration, operational conditions and reagents. Values are based upon half-hourly averages [176, Schenk et al. 2009].
[2] The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].
[3] [176, Schenk et al. 2009].
[4] [117, COM 2007].
[5] [223, Pall Corporation 2009].
[6] Dioxins/furans in the gas phase can be abated when activated carbon is injected into the waste gas upstream of the filter.
NB: NI = no information provided.

Cross-media effects
Consumables associated with ceramic filters are given in Table 3.248.

Table 3.248: Consumables associated with ceramic filters

Consumable	Amount	Comments
Ceramic medium (m^2 per 1 000 Nm^3/h)	NI	—
Compressed air (kPa)	NI	Filter cleaning
Energy (kWh/1 000 Nm^3)	0.2–2	—
Pressure drop (kPa)	25	—
NB: NI = no information provided.		
Source: [176, Schenk et al. 2009].		

The separated dust – possibly mixed with precoating 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 should be disposed of accordingly.

Operational data
Design and maintenance [176, Schenk et al. 2009]
The most important design parameters are the following:

- Incoming gas flow.
- Working temperature and maximum temperature.
- Incoming gas composition.
- Fabric filter load (filter ratio). The fabric filter load is dependent on the type and nature of the cloth material, the dust load and the type and size of the particles. Examples are glass fibre: 60–120 m/h; and PTFE (Teflon): 80–100 m/h.
- The ease of cleaning and the design of the exterior, important for hygiene reasons in the food industry.

Ceramic filters require a relatively high level of maintenance and regular inspection in order to prevent the clogging and poor performance of the filtering elements. For these reasons, it may be decided to lower the process temperatures and to install fabric filters instead, for they are easier to maintain.

Applicability
Ceramic filters are mostly applied for dust removal at high temperatures, especially at combustion installations and gasification systems when coal is used as the fuel, in the waste processing industry, the plastics processing industry, the chemical industry and the glass industry.

Application limits and restrictions are given in Table 3.249.

Table 3.249: Application limits and restrictions associated with ceramic filters

Issue	Limits/restrictions
Typical waste gas flow (Nm^3/h)	300–1 800 000 ([1, 2])
Temperature (°C)	Ceramic filters are particularly adapted for high-temperature filtration (up to about 1 200 °C) and where temperature is variable or subject to surges which could damage conventional fabric media ([2, 3])
Pressure	~ 50 mbar higher or lower than atmospheric ([2])
Dust content (g/Nm^3)	< 20 ([2])
Particle properties	Sticky dusts need to be avoided ([2])
([1]) [58, US EPA 2003]. ([2]) [176, Schenk et al. 2009] ([3]) [154, Startin 2008].	

Advantages and disadvantages are given in Table 3.250.

Table 3.250: Advantages and disadvantages associated with ceramic filters

Advantages	Disadvantages
• In general, ceramic filters provide high abatement efficiencies for coarse and fine particles (ceramic filters generally achieve better efficiencies than fabric filters) • Efficiency and pressure drop of continuously cleaned filters are relatively unaffected by large changes in inlet dust loads • High resistance against abrasive wear from rough particles (for ceramic filters) • Dust is separated dry without using consumables. The separated dust might be reused in the preceding process or recycled • Residual emissions are virtually independent of the intake concentration • Relatively simple operation • Reliability • Modular construction • Can handle high and varying capacities • Can withstand acid and base chemicals	• Vulnerable (ceramic material) • Relatively high pressure drop • Less suitable for wet and/or sticky chemicals • There is an explosion risk in case of flammable chemicals • Baghouse fires are possible if very hot particles are released from furnaces or because of pyrophoric materials • Takes up a lot of space • Relatively high maintenance and operating costs (ceramic filters are more costly than fabric filters)

Economics

The lifespan of the filtering material is dependent on the design and application [176, Schenk et al. 2009]. Economics associated with ceramic filters are given in Table 3.251.

Table 3.251: Economics associated with ceramic filters

Type of costs	Costs
Investment costs (per 1 000 Nm^3/h)	30 000–55 000
Filter material costs (per 1 000 Nm^3/h)	NI
Operating costs (per 1 000 Nm^3/h)	about EUR 1 000
Waste treatment costs (per t)	EUR 75 (solid, non-hazardous) about EUR 250 (hazardous)
Labour (h/week)	NI
Cost-determining parameters	Gas flow, filtering material, surface pressure
Benefits	Savings in costs of raw materials when reuse/recycling is possible, for instance in the glass industry
NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].	

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.

Pollutants that require an unusually high level of control or that require the unit itself to be constructed of special materials will increase the costs of the system.

Driving force for implementation
The driving forces for implementation include legal requirements and raw material savings.

Example plants
The technique is reported to be widely used in the chemical industry sector as well as in other sectors such as the food, drink and milk industries, the waste processing industry, the metal industry, waste incineration, large combustion plants, ceramics manufacturing and the glass industry.

Reference literature
[9, BASF 1999] [11, InfoMil 1999] [19, HMIP 1994] [56, US EPA 2003] [57, US EPA 2003] [58, US EPA 2003] [117, COM 2007] [154, Startin 2008] [176, Schenk et al. 2009] [223, Pall Corporation 2009] [239, Hage 2009]

3.5.1.4.8 Catalytic filtration

Description
Catalytic filtration is the elimination of gaseous compounds accompanied by particulate separation. It is comparable to the operation of fabric and ceramic filters (see Section 3.5.1.4.7). The distinction is between the filter materials, the catalytic filter being loaded with a catalyst (normally a titanium/vanadium-based catalyst) that destroys pollutants by catalytical gas reaction (e.g. to oxidise dioxins and furans or to reduce NO_X when ammonia or urea is injected). The catalyst is also effective at oxidising VOCs where the operating temperature is sufficiently high (> 220 °C) [154, Startin 2008]. The separated dust is removed and recycled/reused or disposed of separately.

The catalyst filter can consist of an expanded polytetrafluoroethylene (ePTFE) membrane, laminated to a catalytic felt substrate. It can also be made using rigid low-density ceramic filter elements (also called candles) incorporating an integral catalyst [154, Startin 2008].

The catalyst is inserted into the felt substrate. The catalytic filter is installed as a module in a baghouse, shown in Figure 3.97, in such a way that it can easily be fitted to an existing plant.
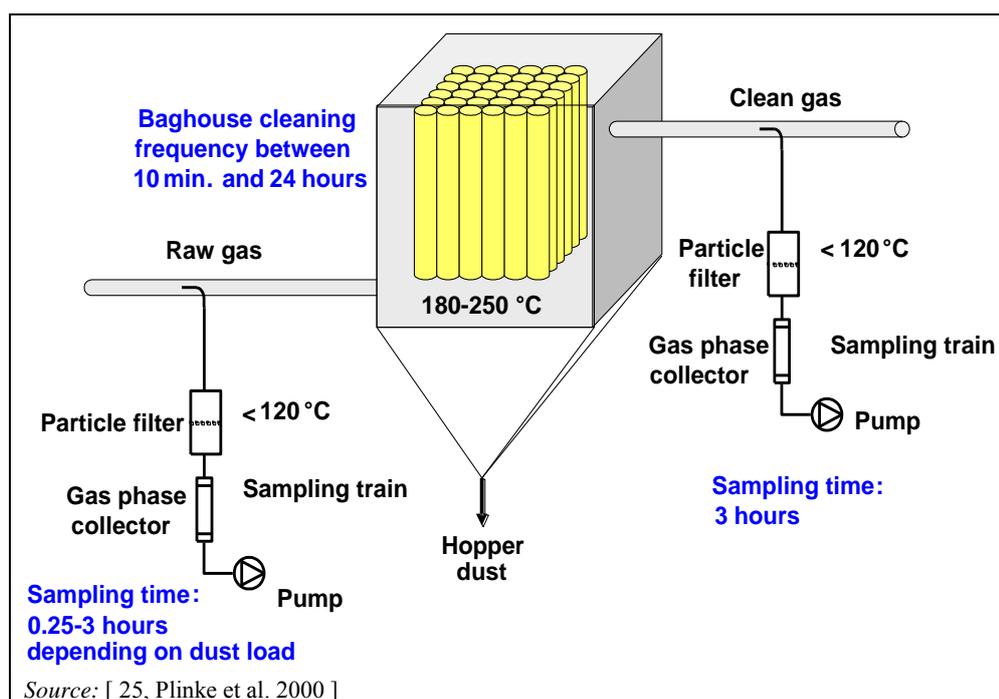

Figure 3.97: Catalytic filter baghouse, including sampling trains

When combined with neutralisation (with the injection, e.g. of sodium bicarbonate or lime, upstream of the catalytic filter) and adsorption systems (downstream of the ceramic and catalytic filters), catalytic filtration can be used to abate acid pollutants (e.g. HCl, SO_2, HF) and heavy metals, in addition to dust, NO_X and dioxins and furans (see Section 5.2.2).

Achieved environmental benefits
Abatement efficiencies and emission levels associated with catalytic filtration are given in Table 3.252**.**

Table 3.252: Abatement efficiencies and emission levels associated with catalytic filtration

Pollutant	Abatement efficiency (%)	Emission level ([1])	Comments
Dust (PM size not identified)	NI	< 1 mg/Nm^3 ([2])	Typical
	> 99 ([3])	NI	Treatment of an incinerator/oxidiser off-gas
NO_X	NI	NI	—
VOCs	NI	NI	—
PCDDs/PCDFs (TEQ)	> 99 ([2, 4])	< 0.004–0.040 ng/Nm^3 ([2])	Waste incinerators/oxidisers
	NI	< 0.075 ng/Nm^3 ([2])	—

([1]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].
([2]) Information from manufacturer.
([3]) Results from a full-scale pilot plant [154, Startin 2008].
([4]) Up to 99.8 % observed.
NB: NI = no information provided.

Cross-media effects
The separated dust possibly mixed with acid gas sorbent material is the only residue for which disposal is required. The filtered dust contains up to 90 % fewer dioxins and furans than when activated carbon is used. The dust is normally classified as non-hazardous waste.

The main utilities and consumables are given in Table 3.253.

Table 3.253: Consumables associated with catalytic filtration

Consumable	Amount	Comments
Filter material	NI	Working life of filter and catalyst about 5 years or even longer
Catalyst	NI	
Energy (kWh/1 000 Nm^3)	NI	—
Pressure drop (kPa)	NI	—
NB: NI = no information provided.		

Operational data
Monitoring [19, HMIP 1994]
Performance and maintenance should be monitored carefully. The mass emission needed 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, for example, on 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 whether 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.

Applicability
Catalytic filtration is used to separate particulates and eliminate hazardous contaminants from the gaseous phase. The chief contaminants this technique is applied for are dioxins and furans (PCDDs/PCDFs). However, other contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated benzenes, polychlorinated biphenyls (PCBs), VOCs and chlorinated phenols can be eliminated as well.

Application limits and restrictions are given in Table 3.254.

Table 3.254: Application limits and restrictions associated with catalytic filtration

Issue	Limits/restrictions
Recommended continuous operating temperature range	160–260 ºC ([1]) if fabric is used as the filter medium. Up to 450 ºC if ceramic is used as the filter medium
Ammonia content	< 200 ppm
Sulphur oxides content	< 50 ppm
Moisture content	5–35 %
Filtration velocity	48–84 m/h
Critical substances	Deactivation of the catalyst, e.g. by arsenic, potassium, calcium, sulphur
([1]) 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 as low as 155 °C.	

Advantages and disadvantages are given in Table 3.255.

Table 3.255: Advantages and disadvantages associated with catalytic filtration

Advantages	Disadvantages
• Destruction of hazardous gaseous compounds without contaminated residues • Reduction in the total release of hazardous pollutants to the environment • Easily retrofittable • 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 if fabric is used as the filter medium, and up to about 450 ºC if ceramic is used as the filter medium • Although the filter removes organics in general, and dioxins and furans specifically at all temperatures, a minimum continuous operating temperature of about 155 °C is recommended for the adequate destruction of dioxins and furans. At lower temperatures, they are adsorbed by the catalyst

Economics
Some cost elements can be found in Section 5.2.2.

Driving force for implementation
Driving forces for implementation include:

- reducing the costs of abatement and increasing depollution efficiency;
- fulfilling environmental legislation.

Example plants
The technique is reported to be used for waste incineration and the processing of metals.

Reference literature
[19, HMIP 1994] [25, Plinke et al. 2000] [154, Startin 2008]

3.5.1.4.9 Two-stage dust filter

Description
The two-stage dust filter contains metal gauze as the 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 into the system. The dust drops to the bottom of the chamber where it has to be removed. An example is shown in Figure 3.98.

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 negated because of the two-stage system.

Source: [11, InfoMil 1999]
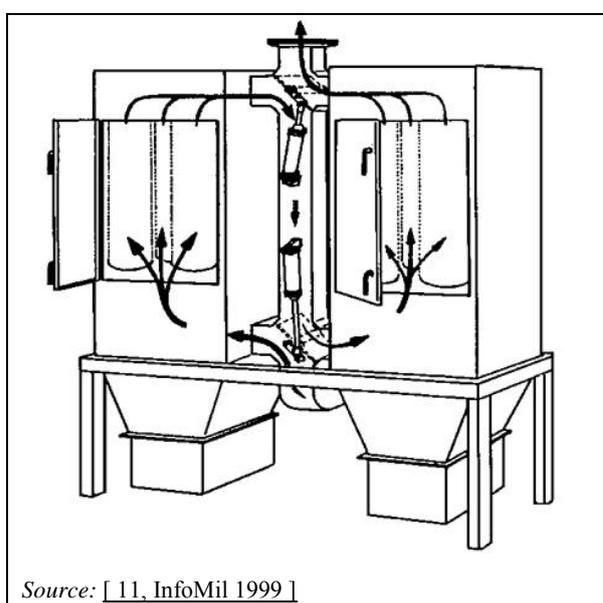
Figure 3.98: Two-stage dust filter

A special variant is the metal mesh filter with recaking process, which is illustrated in Figure 3.99. 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. Under normal operation, the filter works with only some of the filter chambers, while the others are on standby (in the example three chambers are working, the fourth is on standby). The filter continues in this mode until a cleaning cycle has been signalled. Then the previously cleaned and recaked standby chambers come online. The chamber needing cleaning is taken offline and isolated for pulse cleaning, and the dust collected in the dust hopper below. When the cleaning

process is finished, the dust-laden gas is circulated to the recently 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 backup filters to control leakages. When the recaking is complete, the chamber switches to standby mode to replace the next chambers that need cleaning.

Source: [95, Parftec 1999]
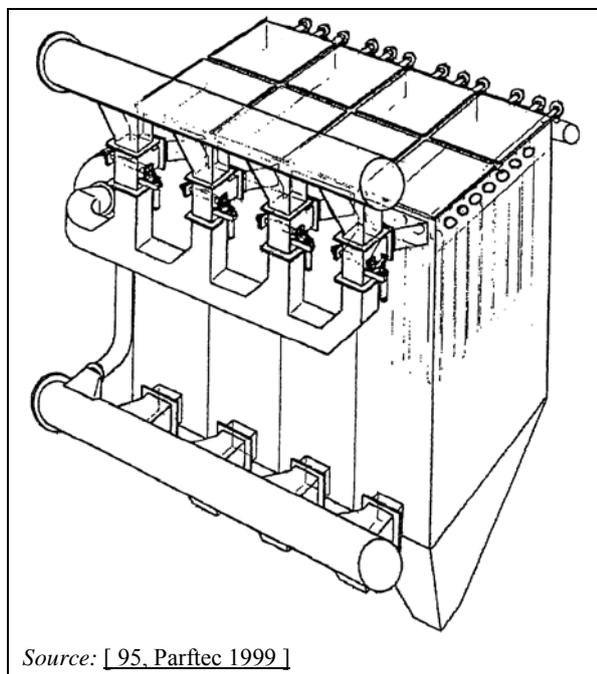
Figure 3.99: Metal mesh filter with recaking process

Systems with an elevated risk, such as of explosion and fire, have to be equipped with safety facilities, e.g. an explosion hatch or sprinkler system.

Achieved environmental benefits
Emission levels associated with two-stage dust filters are given in Table 3.256.

Table 3.256: Emission levels associated with two-stage dust filters

Pollutant	Emission level ([1]) (mg/Nm^3)
Dust (PM size not identified)	1–20
([1]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting.	
Source: [176, Schenk et al. 2009].	

The dust emission of a two-stage dust filter with metal gauze as the filter medium is virtually independent of the inlet load.

Cross-media effects
Consumables associated with two-stage dust filters are given in Table 3.257.

Table 3.257: Consumables associated with two-stage dust filters

Consumable	Amount	Comments
Filter material (metallic gauze or mesh)	NI	—
Compressed air (0.3–0.7 MPa)	NI	Filter cleaning
Energy (kWh/1 000 Nm^3)	1.5	—
Pressure drop (kPa)	0.5–2.5	—
NB: NI = no information provided.		
Source: [11, InfoMil 1999].		

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.

Operational data

Design and maintenance

The most important design parameters are the incoming gas flow and speed when travelling through the filtering material and the filters. Because this filtering material can handle a bigger load than a conventional fabric filter, less filtering surface is required which may result in gains in space. However, because of the fact that this is a two-stage system this advantage is nullified. It is claimed that the additional space in the two-stage system is entirely compensated by the higher filter load.

Monitoring [19, HMIP 1994]

Performance and maintenance have to be carefully monitored. 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, for example, on 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.

Applicability

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.

Application limits and restrictions are given in Table 3.258.

Table 3.258: Application limits and restrictions associated with two-stage dust filters

Issue	Limits/restrictions
Typical waste gas flow (Nm^3/h)	Up to 75 000 per module ([1])
Temperature (°C)	Up to approximately 500
Pressure	Atmospheric ([1])
Pressure drop (mbar)	~ 25 ([2])
Dust content (g/Nm^3)	No restrictions
([1]) [11, InfoMil 1999].	
([2]) [176, Schenk et al. 2009].	

Advantages and disadvantages are given in Table 3.259.

Table 3.259: Advantages and disadvantages associated with two-stage dust filters

Advantages	Disadvantages
• High abatement efficiency for dust • Material recovery is possible • Ventilated air reusable as intake air • Modular structure • Filtering material rarely needs replacement; steel-only design • Filter load higher than for a fabric or a compact filter • Also applicable for damp, sticky, fibrous or static dust • Can withstand high temperatures (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 • Frequent switching between the two compartments (with a normal two-stage filter) • Valve control necessary in a dusty environment • There is an explosion risk

Economics
Economics associated with two-stage dust filters are given in Table 3.260.

Table 3.260: Economics associated with two-stage dust filters

Type of costs	Costs	Comments
Investment costs (per 1 000 Nm³/h)	EUR 40 000	–

Operating costs:
    Labour (h/week)
    Utilities (kWh/1 000 Nm³/h)
	~ 2
	~ 1.5
		–

Waste treatment (EUR/t)	150–250	For toxic waste
Cost-determining parameters	Gas flow, pressure drop, waste treatment	
Benefits	Savings in costs of raw materials when reuse/recycling is possible	
NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].		

Driving force for implementation
The driving forces for implementation include legal requirements and raw material savings.

Example plants
The technique is reported to be widely used in the chemical industry sector as well as in other sectors such as the waste processing industry and refineries.

Reference literature
[11, InfoMil 1999] [19, HMIP 1994] [95, Parftec 1999] [176, Schenk et al. 2009]

3.5.1.4.10   Absolute filter

Description
In absolute filters (e.g. HEPA = high-efficiency particle air filter, ULPA = ultra-low penetration air filter), the filter medium is paper or matted glass fibre with a 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 prefiltering for large diameter particulate matter, hence absolute filter systems are generally the final component in a removal system for particulate matter. This is especially important when the aim is to filter ultrafine or specific nanoparticles arising, for example, from nanomaterial manufacturing processes.

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. A 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, absolute filters are mainly used at lower airflow rates and lower particulate loadings than baghouse designs. Once the airflow rate through the filter system decreases to an unacceptable point, the filter must be replaced. They are generally not cleaned, because the cleaning action may cause leakage of the filter medium.

A schematic of an absolute filter is shown in Figure 3.100.

Source: [176, Schenk et al. 2009]
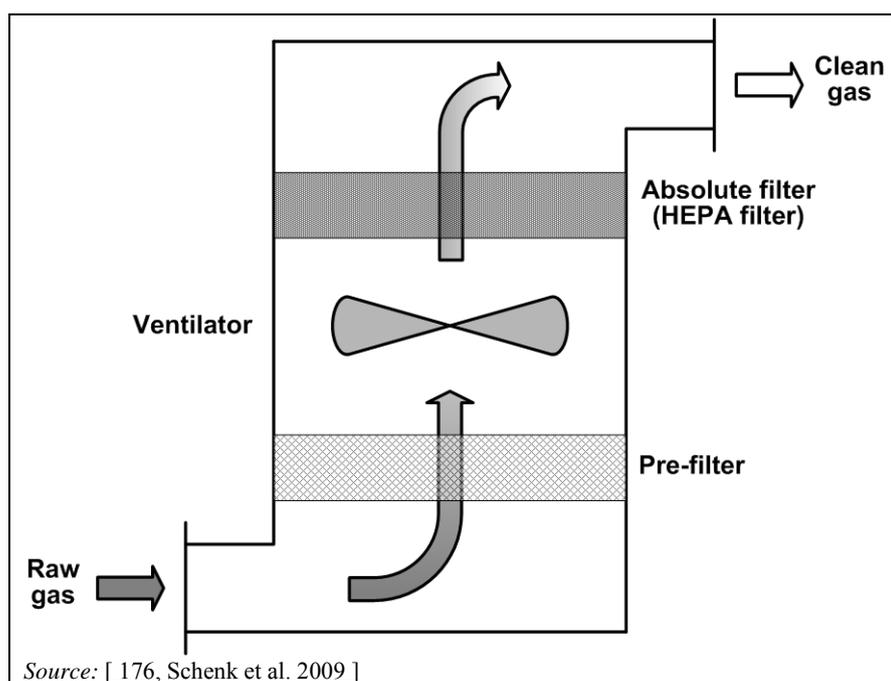
Figure 3.100: Absolute filter

Achieved environmental benefits
Absolute filters are applicable for the removal of dust particles of $PM_{0.12–0.3}$, nanoparticles (diameter between 0.1 µm and 0.001 µm) and for toxic or dangerous particles, like most heavy metals. Absolute filters are often used for the filtration of inside air in locations where a good air quality is necessary.

Abatement efficiencies and emission levels associated with absolute filters are given in Table 3.261.

Table 3.261: Abatement efficiencies and emission levels associated with absolute filters

Pollutant	Abatement efficiency ([1]) (%)	Emission level (mg/Nm^3)
PM	> 99.999 ([2])	> 0.000 1 ([3])
PM$_{0.01}$	> 99.99 ([2, 4])	NI
PM$_{0.1}$	> 99.999 9 ([4]) > 99.999 ([2])	NI
PM$_{>0.3}$	> 99.97 ([2])	NI
PM$_{>0.12}$	> 99.999 5 ([5])	NI
([1]) Depending on the specific configuration and working conditions [176, Schenk et al. 2009]. ([2]) [176, Schenk et al. 2009]. ([3]) [9, BASF 1999]. ([4]) [42, US EPA 2003]. ([5]) Using the ULPA filter variant [176, Schenk et al. 2009]. NB: NI = no information provided.		

Cross-media effects
Consumables associated with absolute filters are given in Table 3.262.

Table 3.262: Consumables associated with absolute filters

Consumable	Amount
Filter material (e.g. paper, glass fibre)	NI
Energy (kWh/1 000 Nm^3)	< 0.1
Pressure drop (kPa)	0.05–0.25
NB: NI = no information provided. *Source:* [11, InfoMil 1999].	

The loaded filter elements should be disposed of as waste. Each module can absorb approximately one kg of dust.

Operational data
Design and maintenance
Absolute filters are the last filtering phase for the removal of dust. Prior to the absolute filter, coarse particles are removed by using another system, e.g. an ESP (see Section 3.5.1.4.4) or a fabric filter (see Section 3.5.1.4.7). Parameters that determine the design of the mechanical aspect and the casing of absolute filters are temperature and pressure. With the most common designs, the filtering units are either right-angled or cylindrical in shape. The filter is folded in order to enlarge the surface.

Monitoring [19, HMIP 1994]
Performance and maintenance have to be carefully monitored. The mass emissions 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, for example, on 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 airflow, the filter should be replaced and disposed of.

Applicability
Absolute filters are typically applicable to submicron particulate matter of PM$_{0.12–0.3}$ as well as hazardous air pollutants that are in particulate form, such as most heavy metals (except mercury). Some absolute filters can even abate nanoparticles (diameter between 0.1 μm and 0.001 μm).

Absolute filters are best applied in situations where high collection efficiency of submicron particulate matter is required, and 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.

Application limits and restrictions are given in Table 3.263.

Table 3.263: Application limits and restrictions associated with absolute filters

Issue	Limits/restrictions
Waste gas flow (Nm^3/h)	100–360 per module ([1, 2])
Temperature (°C)	< 200 ([1, 2]) (commercial HEPA) < 530 ([1, 2]) (ceramic or glass packing) Above dew point of waste gas
Pressure	Atmospheric ([1])
Pressure drop (mbar)	NI
Dust content (g/Nm^3)	1–30 ([1, 2]) < 2 ([3])
Relative humidity (%)	< 95 ([1, 2])
([1]) [176, Schenk et al. 2009]. ([2]) [42, US EPA 2003]. ([3]) [9, BASF 1999]. NB: NI = no information provided.	

Absolute filters require prefiltering to remove large particulate matter (such as cyclones or Venturi scrubbers to reduce large PM or standard baghouse or cartridge filters to filter out particulate matter > PM$_{2.5}$).

Advantages and disadvantages are given in Table 3.264.

Table 3.264: Advantages and disadvantages associated with absolute filters

Advantages	Disadvantages
• Abatement of submicron particles of fine dust is possible • Very high abatement efficiency with very low residual emission • Outlet air is very clean and can be recirculated within the plant • Modular structure • Not sensitive to small fluctuations in the waste gas stream • Relatively simple operation • Usually not sensitive to corrosion problems	• Care has to be taken with explosive hazards • High maintenance and frequent filter replacement required • Not suitable for the abatement of wet dust • Not suitable for high dust loads (except if prefiltration is carried out) • Glass fibre medium is not suitable for waste gases which contain alkalis

Economics
Economics associated with absolute filters are given in Table 3.265.

Table 3.265: Economics associated with absolute filters

Type of costs	Costs	Comments
Investment costs (per 1 000 Nm³/h)	EUR 2 400–3 200 (¹)	—
Annual operating costs	EUR (2 500 + 60 × flow/1 000) (²)	Application-specific
Labour	About 2 hours per week	—
Annual consumables (per 1 000 Nm³/h)	EUR 100–190 (¹)	—
Cost-determining parameters	Gas flow, filtering material	
	None	
(¹) [176, Schenk et al. 2009]. (²) [11, InfoMil 1999]. NB: NI = no information provided.		

Driving force for implementation
The driving forces for implementation include legal requirements and raw material savings.

Example plants
The technique is reported to be used in the chemical industry sector as well as in other sectors such as the pharmaceutical and biochemical industry, the food industry, the photographic industry, the electronic sector and the nuclear industry.

Reference literature
[9, BASF 1999] [11, InfoMil 1999] [19, HMIP 1994] [42, US EPA 2003] [176, Schenk et al. 2009]

3.5.1.4.11 High-efficiency air filter (HEAF)

Description
A 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 preset value of pressure difference is reached, the filter fabric has to be replaced by a new, 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 (see Section 3.5.1.4.12), which separates 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 (see Section 3.5.1.4.12).

Achieved environmental benefits
Abatement efficiencies associated with high-efficiency air filters are given in Table 3.266.

Table 3.266: Abatement efficiencies associated with high-efficiency air filters

Pollutant	Abatement efficiency (%)
Droplets	99
Aerosols	99
Source: [11, InfoMil 1999].	

Cross-media effects
Consumables associated with high-efficiency air filters are given in Table 3.267.

Table 3.267: Consumables associated with high-efficiency air filters

Consumable	Amount
Filter material	NI
Energy (kWh/1 000 Nm^3)	< 0.1
Pressure drop (kPa)	8
NB: NI = no information provided.	
Source: [11, InfoMil 1999].	

Residues to be disposed of are the loaded filter rolls which contain the contaminants separated as droplets, aerosols and dust. They should be disposed of as chemical or hazardous waste and are usually sent to waste incineration.

Operational data
No information provided.

Applicability
HEAF are normally applied to remove aerosols such as oil, plasticisers and condensable VOCs.

Application limits and restrictions are given in Table 3.268.

Table 3.268: Application limits and restrictions associated with high-efficiency air filters

Issue	Limits/restrictions
Typical waste gas flow (Nm^3/h)	Up to 25 000
Pressure	Atmospheric
Source: [11, InfoMil 1999].	

Advantages and disadvantages are given in Table 3.269.

Table 3.269: Advantages and disadvantages associated with high-efficiency air filters

Advantages	Disadvantages
• Continuous process • Suitable for highly viscous droplets	• High pressure drop

Economics
Economics associated with high-efficiency air filters are given in Table 3.270.

Table 3.270: Economics associated with high-efficiency air filters

Type of costs	Costs	Comments
Investment costs (per 1 000 Nm^3/h)	EUR 5 700–8 000	─
Operating costs (per 1 000 Nm^3/h)	About EUR 3 000	About 2.5 hours per week
Source: [11, InfoMil 1999].		

Driving force for implementation
The driving forces for implementation include legal requirements and raw material savings.

Example plants
No information provided.

Reference literature
[11, InfoMil 1999]

3.5.1.4.12 Mist filter

Description
The most common mist filters (mist eliminators, demisters) are mesh pad filters. 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. It works by mechanical impingement and is 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, regular washing is necessary. 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 no gaps remain 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.

Demisters often form an integrated part of other techniques, for example gas scrubbers.

A schematic of a typical mist filter is shown in Figure 3.101.
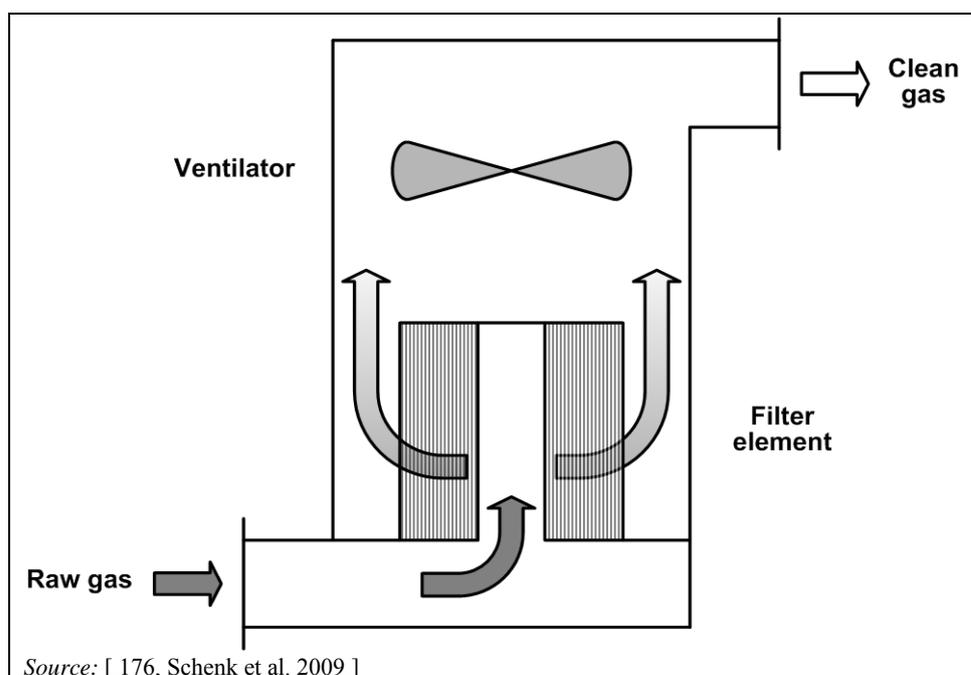
Figure 3.101:   Mist filter

Achieved environmental benefits
Abatement efficiencies associated with mist filters are given in Table 3.271.

Table 3.271: Abatement efficiencies associated with mist filters

Pollutant	Abatement efficiency ([1]) (%)	Comments
Dust, droplets and aerosols	99	Filtering elements with a small mesh for the removal of dust (1–3 μm) are more efficient for the smallest drops, but the chance of clogging increases. Remaining emissions would consist of a scrubbing liquid with removed dust and polluted filtering material
([1]) Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages.		
Source: [176, Schenk et al. 2009].		

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 has a functional liquid drainage capacity. This mesh pad configuration is usually effective on particles of 5–10 μm in diameter.

Cross-media effects
Consumables associated with mist filters are given in Table 3.272.

Table 3.272: Consumables associated with mist filters

Consumable	Amount	Comments
Filter material	NI	—
Washing liquid	NI	For cleaning
Energy (kWh/1 000 Nm^3)	NI	—
Pressure drop (kPa)	2.5	Normal
	9.0	Large loads
NB: NI = no information provided.		
Source: [176, Schenk et al. 2009].		

Residues to be disposed of are the washing liquid, which contains filtered dust and the loaded filter material. The washing liquid should either undergo waste water treatment or should be 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.

Operational data
Monitoring
The pressure drop of each individual stage of the mist filter needs to be monitored, e.g. by magnehelic or photohelic gauges.

Applicability
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 that are soluble in liquids. Owing to clogging, they are less suitable for solid dusts and greasy vapours. They protect equipment from solid/liquid dust particles and 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 savings and economics in many processes that involve 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 for using these kinds 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-stage or four-stage unit, using a monofilament and voids configuration in the first stages and gradually decreasing the 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 contaminants 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 being carried into the clean gas discharging into the air. A mist filter is situated at the top 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 (see Section 3.5.1.2.4) or distillation equipment (see Section 3.3.2.3.4.14) need to be reduced.

Application limits and restrictions are given in Table 3.273

Table 3.273: Application limits and restrictions associated with mist filters

Issue	Limits/restrictions
Typical waste gas flow (Nm^3/h)	Up to 150 000
Temperature (°C)	< 170
Pressure (mbar)	NI
Dust content (mg/Nm^3)	< 1
Aerosols level	A few g/Nm^3
NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].	

Advantages and disadvantages are given in Table 3.274.

Table 3.274: Advantages and disadvantages associated with mist filters

Advantages	Disadvantages
• Self-cleaning systems for the collection of liquids • Suitable for filtration of liquid aerosols, also as a primary device	• The cleaning of the filter results in a contaminated washing liquid • Possibility of high pressure drop when separating solid dust particles • Clogging risk due to presence of dust particles and fatty fumes

Economics
Economics associated with mist filters are given in Table 3.275.

Table 3.275: Economics associated with mist filters

Type of costs	Costs	Comments
Investment costs (per 1 000 Nm^3/h)	EUR < 2 300	─
Operating costs	EUR 2 500 + (450 × flow/1 000)	─
Labour	Approximately 2 hours per week	─
Consumables (per year and per 1 000 Nm^3/h)	EUR 250–600	Filtering material
Cost-determining parameters	Gas flow, pressure drop, filtering element	
Benefits	None	
NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].		

Driving force for implementation
Driving forces for implementing mist filters are reduction of aerosols and droplets, protection of equipment from solid/liquid dust particles and prevention against wear and friction on blower bearings and housings.

Example plants
The technique is reported to be used in the chemical industry sector as well as in other sectors such as the textile industry, the food industry and the plastics processing industry.

Reference literature
[176, Schenk et al. 2009]

3.5.1.5 Recovery and abatement techniques for inorganic compounds

3.5.1.5.1 Overview

Techniques to recover/abate SO_X (flue-gas desulphurisation = FGD), HF, and HCl include:

- wet scrubbing (see Sections 3.5.1.2.4 and 3.5.1.4.5);
- sorbent injection (see Section 3.5.1.5.2).

Techniques to abate NO_X include:

- selective reduction, catalytic (SCR) or non-catalytic (SNCR) (see Section 3.5.1.5.3);
- non-selective catalytic reduction (NSCR) (see Section 3.5.1.5.4).

3.5.1.5.2 Sorbent injection

Description
The reaction principle of 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 (often with a filter, e.g. bag filter).

The most frequently used sorbents are:

- limestone and its derivatives;
- dolomite and its derivatives;
- sodium hydrogen carbonate (sodium bicarbonate);
- sodium carbonate (soda ash).

The choice of the sorbent depends on the process conditions (temperature, flow rate, humidity, pollutant contents) and its availability.

These sorbents are also effective in removing other acid gases, particularly hydrogen chloride (HCl) and fluoride (HF). If these acid gases are intended to be recovered, the waste gas needs to be pretreated (water scrubbing, see Section 3.5.1.2.4).

There are three types of sorbent injection techniques:

- dry sorbent injection;
- semi-dry (or semi-wet) sorbent injection;
- wet sorbent injection (see also Section 3.5.1.2.4).

With **dry sorbent injection**, the fine powdered sorbent (when sodium bicarbonate is used, it is often ground on site to the optimal granulometry) is either injected into the waste gas stream or added to a reaction tower, the latter being the more efficient method. The sorbent can be injected into the waste gas stream at various positions according to the temperature and conditions at which it is most reactive. This is illustrated in Figure 3.102.
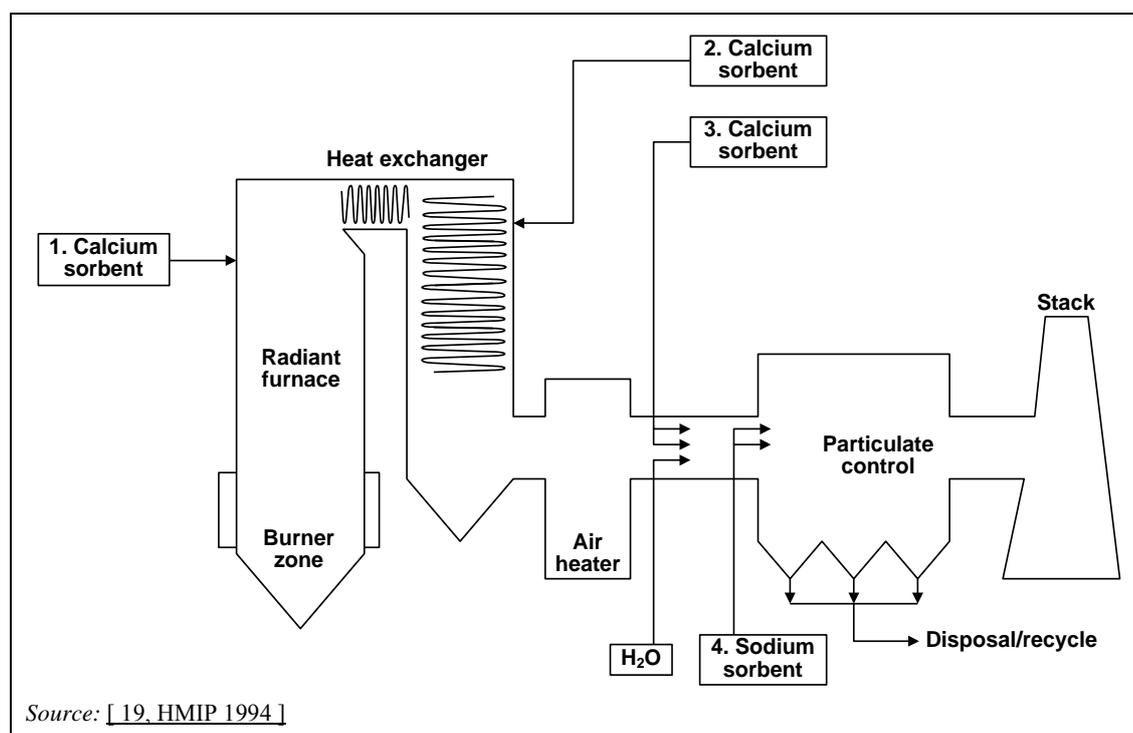
Source: [19, HMIP 1994]

Figure 3.102:   **Dry sorbent injection for sulphur dioxide removal (injection positions)**

Commonly used injection positions and adequate sorbents are [19, HMIP 1994]:

- furnace injection of limestone at temperatures between 1 100 °C and 1 250 ºC;
- heat exchanger injection of slaked lime at temperatures of approximately 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 the heat exchanger and the particulate abatement device, at a temperature range between 140 ºC and 250 ºC or, when the filter medium allows it, up to 400 °C.

Using a bag filter is preferable because the reaction can continue with the unreacted sorbent deposited on the filter media. When an ESP (see Section 3.5.1.4.4) is used, it is preferable to inject the sorbent in a reactor to guarantee a sufficient contact time of a few seconds between the sorbent and the waste gas before the ESP [167, ADEME 1999].

Due to its ability to work at relatively high temperatures and to its very high efficiency with regard to SO_2 abatement, the dry sodium bicarbonate process may be used upstream of a SCR DeNO$_X$ system, without reheating the waste gas before entering the SCR system. This creates energy and cost savings which may be significant.

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 3.103 using a fabric filter for 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 waste gas flowing concurrently);
- associated slurry/liquid equipment (lime slurries or sodium carbonate/bicarbonate solutions);
- a particulate collection device;
- a particulate recycling device.

Figure 3.103: **Spray or semi-dry sorbent injection system**

With **wet sorbent injection**, SO_2 is removed from the waste gas in the absorber by direct contact with a slurry of alkaline sorbent (e.g. aqueous suspension of finely ground limestone, lime slurry, seawater), after having left the particulate control system and passed through a heat exchanger (see also Section 3.5.1.2.4). The scrubbed waste 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.

As limestone injection is one of the most common systems, it is the one described below for illustration purposes.

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 3.104.

Figure 3.104:   Lime milk scrubber

The solid part of the scrubber cycle is principally gypsum with a concentration of 100–120 g/l. Modern combustion units operate with a fairly rich mix, and the oxygen content of the waste gas is 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, the 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 concurrent units that high gas rates reduce the residence time and thus the level of desulphurisation.

To reduce the chloride concentration in the scrubbing liquid to 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 waste gas leaves the 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 updraught in the stack or cooling tower are required.

The adequate particle abatement technique to remove the dry material both from dry and semi-dry systems is the use of an ESP (see Section 3.5.1.4.4) or fabric filters (see Section 3.5.1.4.7). If fabric filters are used, the flue-gas normally requires cooling, either by a heat exchanger or cooling air, to keep the temperature below 250 °C (except with fabrics suitable for higher temperatures, such as ceramics or metal gauze/mesh).

Achieved environmental benefits
The temperature at which maximum abatement efficiency is achieved varies from compound to compound. Furthermore, waste gas pollutants have a different reactivity 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 the reaction temperature. Due to the nature of the gas/solid reaction, the absorption rates are highly dependent on the specific active area of the absorbent, the residence time and the gas temperature at the injection point. For the abatement of HCl, the ideal diameter of the absorbent grain is $d_{90} < 35$ μm while for the abatement of SO_2 with efficiency > 95 %, the ideal diameter is $d_{90} < 20$ μm ('$d_{90} <$' means that 90 % of the absorbent grains have a diameter below the given value in μm). Therefore, it is normally necessary to have an over-stoichiometric ratio of absorbent.

Using lime, the abatement efficiencies for species such as HCl and SO_2 decrease drastically with decreasing temperature and are at a minimum in the range between 200 °C and 280 °C. Below 200 °C, the abatement efficiencies increase and can achieve good results for most pollutants. Using sodium bicarbonate, the abatement efficiencies are optimum between 140 °C and 300 °C. The performances start to decrease under 140 °C when there is no recirculation [213, CEFIC 2009].

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. Different efficiencies under various conditions are given in Table 3.276 to Table 3.280.

Table 3.276: Dry sorption abatement efficiencies and emission levels for lime as a sorbent with different temperatures and dust abatement systems

Pollutant	Abatement efficiency ([1, 2]) (%)			Emission level (mg/Nm³)
	ESP		Bag filter	
	About 400 °C	200–280 °C	130–240 °C	
SO_2 ([2])	50	10	10–70	NI
SO_3 ([3])	80	90	95	NI
HCl ([2])	70	35	80	< 10
HF ([2])	95	95	95	< 1
([1]) Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009]. ([2]) [176, Schenk et al. 2009]. ([3]) [72, VDI 1999]. NB: NI = no information provided.				

Table 3.277: Dry sorption stoichiometric ratios and abatement efficiencies for sodium bicarbonate as a sorbent and dust abatement systems

Pollutant	Stoichiometric ratio		Abatement efficiency ([1]) (%)	
	ESP	Bag filter	ESP	Bag filter
SO_2	1.4–1.7	1.2–1.3	> 90	> 95
SO_3			> 95	> 98
HCl			> 95	> 98
HF			> 90	> 95
([1]) Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages. *Source:* [162, CEFIC 2009].				

Table 3.278: **Dry sorption SO$_X$ abatement efficiencies for lime as a sorbent with different temperature ranges and Ca/S molar ratios**

Molar ratio Ca/S	SO$_X$ abatement efficiency (%)	
	130–140 °C	170–180 °C
1	30	22
2	50	40
3	70	55
Source: [167, ADEME 1999].		

Table 3.279: **Semi-dry sorption SO$_X$ abatement efficiencies for lime as a sorbent with different Ca/S molar ratios**

Molar ratio Ca/S	SO$_X$ abatement efficiency (%)
1	80
1.5	90
2	92
Source: [167, ADEME 1999].	

Table 3.280: **Dry and semi-dry sorption abatement efficiencies for sodium carbonate as a sorbent**

Pollutant	Abatement efficiencies (%)	
	Dry sorption ([1])	Semi-dry sorption
SO$_2$	< 50	90–95
SO$_3$	90	NI
HCl	50–75	> 90
HF	10–40	> 85
([1]) Temperature range 300–400 °C.		
NB: NI = no information provided.		

Abatement efficiencies and emission levels associated with sorbent injection are given in Table 3.281.

Table 3.281: Abatement efficiencies and emission levels associated with sorbent injection

Pollutant	Dry sorption		Semi-dry sorption		Wet sorption	
	Abatement efficiency [1] (%)	Emission level [2, 3] (mg/Nm³)	Abatement efficiency [1] (%)	Emission level [3] (mg/Nm³)	Abatement efficiency [1] (%)	Emission level [3] (mg/Nm³)
SO$_X$	10–70 [4]	< 40	85–> 90 [5, 6]	< 40	90–97 [7, 8]	< 40 [6]
	90–95 [9]	< 5 [9]	NI	NI	NI	NI
SO$_2$	75–98 [10]	NI	NI	NI	NI	NI
HCl	> 95–> 98 [11]	< 2 [9]–< 10 [6]	> 99 [5]	< 10 [6]	NI	< 10 [6]
	75–98 [10]	NI	NI	NI	NI	NI
HF	> 90–> 95 [11]	< 1 [6]	> 85 [4]	< 1 [6]	NI	< 1 [6]
	75–98 [10]	NI	NI	NI	NI	NI
NO$_X$	35–50 [10]	NI	NI	NI	NI	NI

[1] Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
[2] Achievable emission levels, but normally dry sorption is not used for such low concentrations where wet scrubbing or sorption might be the preferred technique.
[3] The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].
[4] [176, Schenk et al. 2009].
[5] [19, HMIP 1994].
[6] [11, InfoMil 1999].
[7] Dependent on L/G ratio (90 % with 8 l/Nm³, 95 % with 14 l/Nm³, 97 % with 20 l/Nm³).
[8] [240, Weilert 2006].
[9] With sodium bicarbonate injection [160, CEFIC 2009].
[10] With sodium bicarbonate injection (stoichiometric ratio between 0.8 and 1.2) and ratio SO$_2$/NO$_X$ = 8 [167, ADEME 1999].
[11] With sodium bicarbonate injection [162, CEFIC 2009].
NB: NI = no information provided.

A reduction of NO$_X$ emissions was reported when using sodium carbonate or bicarbonate in the semi-dry process; for sodium bicarbonate the optimal range is between 140 °C and 250 °C [160, CEFIC 2009]. The efficiency depends on the SO$_2$/NO$_X$ ratio. The abatement efficiency is favoured by a high ratio and moderate temperatures [115, COM 2013].

Cross-media effects
Consumables associated with sorbent injection are given in Table 3.282.

Table 3.282: Consumables associated with sorbent injection

Consumable	Amount		
	Dry sorption	Semi-dry sorption	Wet sorption
Sorbent ([1]) (Ca/S molar ratio)	3 or more (for lime)	1.5–3 (for lime)	< 1.1 ([2])
Water ([3]) (l/Nm^3)	NA	0.027–0.04 ([4])	8–20 ([5])
Energy (kWh/1 000 Nm^3)	Dependent on dust removal system	1 ([6])	NI
Pressure drop (kPa)	Dependent on dust removal system	2.5 ([6])	NI
Noise	If the grinding of sorbent is carried out on site without appropriate noise protection measures	NI	NI

([1]) Sodium hydrogen carbonate requires a considerably smaller excess. No excess for sodium bicarbonate until 80 % SO$_2$ abatement; ratio 2Na/S = 1.2–1.3 for 95 % SO$_2$ abatement [162, CEFIC 2009].
([2]) [67, Ullmann's 2000].
([3]) Liquid/gas ratio.
([4]) [19, HMIP 1994].
([5]) 8 l/Nm^3 corresponding to 90 %, desulphurisation, 14 l/Nm^3 to 95 % and 20 l/Nm^3 to 97 %.
([6]) [176, Schenk et al. 2009]; depending on the subsequent dust removal system.
NB: NA = not applicable; NI = no information provided.

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, it has to be disposed of. All pollutants that have not been destroyed during the incineration process are included, such as heavy metal compounds and/or dioxins, depending on the input of the incineration installation. Sometimes the dust is partially recycled.

When sodium bicarbonate is used in dry injection to abate HCl or SO$_2$, residues can be treated and recycled as NaCl brine in soda ash production plants or the sodium sulphate can be recycled in some industries (glass and cement) [160, CEFIC 2009] [228, CWW TWG 2011].

With wet sorption, the residue is gypsum. When combusting fossil fuels (coal, lignite, oil), the gypsum is often of high purity (> 99 % CaSO$_4$ in the solid) [67, Ullmann's 2000], and can be used elsewhere.

Operational data
Design and maintenance [176, Schenk et al. 2009]
Regular inspection of the system is required in order to prevent clogging of the piping and the moving parts and to ensure the good performance of the subsequent filter (e.g. fabric filter, ESP).

Monitoring [19, HMIP 1994]
The performance of the dry sorbent and semi-dry sorbent injection system is assessed by determining the acidic gas concentration and particulate abatement efficiencies.

In the case of variable emissions, sorbent injection is regulated with an online SO$_2$ analyser so as to meet emission limit values and minimise the amount of sorbent used [167, ADEME 1999].

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.

Applicability
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

investment costs for other systems might be very high. Dry injection using sodium bicarbonate can easily be retrofitted to an existing plant [167, ADEME 1999].

To reduce other contaminants (e.g. heavy metals, dioxins/furans), granulated activated carbon (GAC) can be added to the dry sorbent.

Application limits and restrictions are given in Table 3.283.

Table 3.283: Application limits and restrictions associated with sorbent injection

Issue	Limits/restrictions
Typical waste gas flow (Nm^3/h)	10 000–300 000 (dry sorbent)
	Up to 1 000 000 ([1]) (semi-dry sorbent)
	50–500 000 ([1]) (wet sorption)
Temperature (°C)	Temperature limits and restrictions depend in particular on the type of sorbent injection technique, the type of sorbent, and the downstream abatement system, as indicated in the previous paragraphs. For example, at a temperature of 140 °C–300 °C, dry sodium bicarbonate abatement efficiency is considered optimal ([2])
Pressure drop (mbar)	Approximately 25 (semi-dry sorbent)
SO_X concentration	Very wide range, up to 10 000 mg/Nm^3 ([3])
Hydrogen halides (e.g. HCl, HF) concentration	Wide range for dry, semi-dry and wet sorbent injection
([1]) [176, Schenk et al. 2009]. ([2]) [160, CEFIC 2009]. ([3]) [167, ADEME 1999].	

Advantages and disadvantages are given in Table 3.284.

Table 3.284: Advantages and disadvantages associated with sorbent injection

Advantages	Disadvantages
General • Removal of inorganic acidic compounds (SO_X, HCl, HF)	General • Relatively large space required
Dry sorbent injection • No extra installations are necessary since a dust removal system is usually installed • High abatement efficiency can be achieved if a well-designed reaction chamber or tower is installed • Low-cost system compared with others • No waste water produced • A sodium bicarbonate dry injection allows the use of an SCR without reheating the flue-gas • Possible recycling of Na-based residues	Dry sorbent injection • The added sorbent can, by interacting with fly ash, cause fouling of heat exchanger surfaces • Large surplus of sorbent that should be disposed of (larger surplus of sorbent for high removal rate when lime is used compared to when sodium bicarbonate is used) [160, CEFIC 2009]
Semi-dry sorbent injection • Relatively simple installation • Cheaper than wet scrubbing • No waste water produced	Semi-dry sorbent injection • Poor particulate separation performance in the reaction chamber • Humidity can be a problem if a fabric filter is used for subsequent particulate abatement
Wet sorbent injection • Very high efficiencies • Compact equipment • Can operate at relatively high temperatures (50–80 °C) • Indirect monitoring through stoichiometric dosing of chemicals (if pH controlled) • Reusable product, when lime is used (gypsum)	Wet sorbent injection • Significant water usage and generation of waste water • Energy consumption to reheat flue-gas before discharging

Economics

Economics associated with sorbent injection are given in Table 3.285.

Table 3.285: Economics associated with sorbent injection

Type of costs	Costs		
	Dry sorption	**Semi-dry sorption**	**Wet sorption**
Investment costs (per 1 000 Nm^3/h)	Dependent on the dust removal system. Because the boiler or ductwork is used as the capture zone of the pollutants, the investment costs are reduced compared to a wet scrubber	EUR 11 000 based on 100 000 Nm^3/h ([1])	NI
Annual operating costs (per 1 000 Nm^3/h)	EUR 2 500 + 300 × flow/1 000 + sorbent ([1])	EUR 20 000 + 400 × flow/1 000 + sorbent ([1])	NI
Adsorbent (EUR/t)	100–250 ([2, 3])	~ 60 (lime)	NI
Water (l/Nm^3)	NI	0.03–0.04 ([2])	NI
Labour	About 2 hours per week ([2])	1 day per week ([2])	NI
Cost-determining parameters	Flow, pressure drop, pollutant concentration ([2])	Dust removal system	NI
Benefits	None ([2])	NI	NI

([1]) [11, InfoMil 1999].
([2]) [176, Schenk et al. 2009].
([3]) [227, CWW TWG 2009].
NB: NI = no information provided.

Driving force for implementation

Abatement of acidic gas emissions is the main driving force for using the technique.

Example plants

Sorbent injection is used in many plants worldwide, in various industry sectors such as in chemical production, incineration, large combustion plants, glass production, the metal processing industries, and the cement and ceramic industries [160, CEFIC 2009] [176, Schenk et al. 2009].

Reference literature

[11, InfoMil 1999] [19, HMIP 1994] [67, Ullmann's 2000] [72, VDI 1999] [115, COM 2013] [160, CEFIC 2009] [162, CEFIC 2009] [167, ADEME 1999] [176, Schenk et al. 2009] [213, CEFIC 2009] [227, CWW TWG 2009] [228, CWW TWG 2011] [240, Weilert 2006]

3.5.1.5.3   Selective reduction of NO$_X$ (SNCR and SCR)

Description

Selective reduction of NO$_X$ (selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR)) involves the injection of NH$_2$-X compounds (with X = H, CN or CONH$_2$) into the waste gas stream, reducing nitrogen oxides to nitrogen and water. The most common reducing agent is a 25 % aqueous solution of ammonia or pure ammonia. Other reaction agents are urea solutions, nitrolime or cyanamide (NH$_2$CN).

There are different variants of selective NO$_X$ reduction including:

- selective non-catalytic reduction (SNCR);
- selective catalytic reduction (SCR).

When using **SNCR** with ammonia, the reducing agent is injected into the area where the waste gases have reached a temperature typically between 930 ºC and 980 ºC, whereas when using SNCR with urea, it is injected into an area where the gas temperature is between 950 ºC and 1 050 ºC. The injection occurs after combustion and before further 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 slips can also occur, generating aerosols of ammonium chloride and sulphate, which pass through the filter and cause visible white plumes above the stack. The residence time and mixing quality are decisive for the reaction efficiency. Too short a residence time will cause an ammonia slip. The correct amount of injected ammonia is calculated based on the NO value in the raw gas, the targeted NO_X value in the clean gas and the waste gas mass flow. Special attention should be paid to the ammonia distribution and mixing as this is of great importance in achieving low NO_X and ammonia emissions (e.g. nozzle arrangement for ammonia injection, and vortex flow in the reaction chamber for correct mixing) [136, John Zink 2008].

With **SCR**, the waste gas stream and the reducing agent injected are passed over a catalyst, with operation temperatures typically between 200 °C and 500 °C, depending on the catalyst. Lower temperatures can make the catalyst inactive, whereas higher temperatures can cause damage to the catalyst. Typical arrangements of SCR include a heat exchanger and a direct fired heater to reach the right operating temperatures for the catalyst [136, John Zink 2008]. SCR temperature range depends upon SO_X concentration: an excessively high SO_X concentration and a temperature that is too low lead to ammonium bisulphate formation (which can also plug the catalyst [136, John Zink 2008]). About 315 °C is the lower band for applications with SO_2 above 300 mg/Nm^3 [227, CWW TWG 2009]. 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 an ammonia slip. Often the precleaned waste gas has to be preheated before entering the catalytic bed.

The considerably lower temperatures compared to SNCR make it possible to install SCR downstream of other treatment devices such as dust abatement (e.g. fabric filters, see Section 3.5.1.4.7) and FGD units (see Sections 3.5.1.2.4 and 3.5.1.5.2). With this 'cold' DeNO$_X$ 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 to the necessary reaction temperature. The advantage of this procedure is that, because there is no adsorption to dust, there is no potential for an 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 and aluminium oxide as the carrier material with vanadium, tungsten and molybdenum compounds as active material. Some substances can cause the catalyst to lose its efficiency [136, John Zink 2008]:

- Halogens, which can react chemically with the active material (e.g. vanadium) to form products which will evaporate and cause the catalyst to malfunction. Also, concentrations of halogens are normally limited in the waste gas.
- Alkali metals (e.g. Na, K).
- Earth alkali metals (mainly Ca), which will become toxic substances when SO_3 is also present in the waste gas (i.e. formation of $CaSO_3$ which can block the surface of the catalyst).

- Phosphates.
- Arsenic and other heavy metals.
- Sulphur, which must be limited at the entry of a catalyst. If the waste gas contains SO_3 a minimum reactor temperature of $> 300\,°C$ should be held to avoid condensation of ammonium bisulphate which also plugs the pores of the catalyst.

There are other techniques that treat sulphur dioxide and NO_X in either consecutive or simultaneous operations, such as [6, VCI 1995]:

- the DeSONO$_X$ 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 with sulphuric acid;
- the 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.

Achieved environmental benefits
Abatement efficiencies and emission levels associated with the selective reduction of NO_X are given in Table 3.286.

Table 3.286: Abatement efficiencies and emission levels associated with the selective reduction of NO_X

Pollutant	SNCR		SCR	
	Abatement efficiency ([1, 2]) (%)	Emission level ([3]) (mg/Nm^3)	Abatement efficiency ([1]) (%)	Emission level ([3]) (mg/Nm^3)
NO_X (gas boilers/heaters)	40–80 ([4]) 25–70 ([5])	60–70 ([4])	90–94 ([4]) 80–95 ([5])	< 20
NO_X (liquid fuel boilers/heaters)	40–80 ([4]) 25–70 ([5])	60–70 ([4])	90–94 ([4]) 80–95 ([5])	55–150
NO_X (from nitric acid production)	NI	NI	80–95 ([6]) 84 ([7])	150–200 ([6])
NH$_3$	NA	< 5 ([8]) 2–20 ([5])	NA	< 5 ([8]) 2–20 ([5])

([1]) Efficiency depends on the specific plant configuration, operational conditions; the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([2]) When retrofitting SNCR, the lower range of the abatement efficiency typically applies, as it is more difficult to design for the optimum residence time and temperature range [228, CWW TWG 2011].
([3]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].
([4]) [176, Schenk et al. 2009].
([5]) Removal percentage is dependent on the inlet concentration, especially if inlet concentration is low (reported by CEFIC [227, CWW TWG 2009]).
([6]) [92, InfoMil 1999].
([7]) Average performance of 12 nitric acid plants in France in 2002 [157, ADEME 2004].
([8]) Measurements from Austria; values for new catalysts, but higher NH$_3$ emissions occur as the catalyst ages.
NB: NA = not applicable; NI = no information provided.

Cross-media effects
Consumables associated with the selective reduction of NO_X are given in Table 3.287.

Table 3.287: Consumables associated with the selective reduction of NO_X

Consumable	Amount	
	SNCR	SCR
Ammonia ([1]) (kg/t of NO_X removed)	570 ([2])	370–450 ([2, 3])
Catalyst	Not relevant	NI
Steam to evaporate ammonia before it is injected (from aqueous solution)	NI	NI
Energy ([4]) (kWh/1 000 Nm^3)	Low; only for the injection of reducing agent ([5])	Low; for the heating of smoke gases in a 'low-dust' installation ([5])
Pressure drop (kPa)	NI	0.1–1 ([2])
([1]) Depending on the amount of NO_X reduced [102, COM 2007]. ([2]) [11, InfoMil 1999]. ([3]) Upper value information from Italy. ([4]) Energy consumption only for the dosing of ammonia or urea [176, Schenk et al. 2009]. ([5]) [176, Schenk et al. 2009]. NB: NI = no information provided.		

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.
Ammonia slip levels when using SCR and SNCR are given in Table 3.286.

Nitrous oxide (N_2O) may be formed (in particular from older catalysts [102, COM 2007]) when using SCR [176, Schenk et al. 2009]. The formation of N_2O is increased as the vanadium loading in the catalyst is raised [178, Yates et al. 2005].

In 'high-dust' sequences (i.e. SCR located directly after the boiler), the fly ashes are loaded with NH_3 [176, Schenk et al. 2009].

Operational data
Monitoring
The performance of the SNCR or SCR systems can be monitored by analysing the nitrogen oxides content before and after treatment and the ammonia and oxygen content of the effluent gas stream.

The temperature and pressure drop (with SCR) are routinely monitored.

Applicability
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.

When SCR is used, any SO_2 present in the waste gas might be oxidised to SO_3 over the catalyst. SO_3 reacts with ammonia to form ammonium sulphate. The ammonium sulphate might clog the catalyst and be emitted as an aerosol that can be difficult to remove [176, Schenk et al. 2009]. A way to avoid/reduce this phenomenon is to operate the SCR system at higher operating temperatures.

Application limits and restrictions are given in Table 3.288.

Table 3.288: Application limits and restrictions associated with the selective reduction of NO_X

Issue	Limits/restrictions	
	SNCR	SCR
Typical waste gas flow (Nm^3/h)	> 10 000–< 200 000	Up to 1 000 000
NO_X concentration	In the range of g/Nm^3	In the range of g/Nm^3
Temperature (°C)	930–980 (when using ammonia)	200–500 (dependent on catalyst); fluctuations of about 90°C are acceptable ([1])
Pressure	Atmospheric	Atmospheric
Pressure drop (mbar)	NI	< 10
Residence time (s)	1–2	NI
Dust concentration (g/Nm^3)	NI	Some
NO_X concentration (g/Nm^3)	NI	< 3 (including diesel motors)
NH_3/NO_X molar ratio	< 1.2	< 1.1
NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].		

SNCR performance can be negatively affected by the high concentration of bound nitrogen in the inlet gas, or when the NO_X concentration in the inlet of the SNCR system is significantly higher than 2 000 mg/Nm^3. Also, in cases where there is a very low concentration of bound nitrogen and therefore small amounts of NO_X at the entry of the SNCR system, the NO_X reduction rate can become worse [136, John Zink 2008].

Advantages and disadvantages are given in Table 3.289.

Table 3.289: Advantages and disadvantages associated with the selective reduction of NO_X

Advantages	Disadvantages
General • Both SNCR and SCR are generally proven techniques	General • Special safety provisions are necessary when liquid ammonia systems are used
SNCR • Good NO_X reduction achievable • Relatively simple installation, though much know-how is needed to locate the ammonia injectors properly • Low investment costs compared to alternatives • Low energy requirements • Low space requirements [176, Schenk et al. 2009] • Waste gas with a high dust concentration can also be treated [176, Schenk et al. 2009]	SNCR • High temperature is necessary, and the optimal reaction temperature is in a precise range [176, Schenk et al. 2009] • Fly ashes contain ammonia • Outside the operational condition range (temperature, NH_3/NO_X ratio, residence time) an ammonia slip or an increased NO_X emission can occur • Not suited for sources with a low NO_X level • When applied to combustion devices with variable loads, difficulty in achieving high and constant NO_X abatement efficiency
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 • Capable of operating within a low temperature range and hence lower energy consumption for heating • Because of lower dust content, lower ammonia slip • Relatively easy installation; no modifications to the upstream incinerators/oxidisers are generally necessary [176, Schenk et al. 2009] (in some cases modifications to incinerators are needed to allow required temperature range for SCR [227, CWW TWG 2009])	SCR • Outside the operational condition range (temperature, NH_3/NO_X ratio, residence time), an ammonia slip, and a lower NO_X destruction efficiency can occur • Pressure drop to be considered • Considerable space requirements • Relatively high investment costs compared with SNCR • Costs of the catalyst (potential clogging, poisoning and possible erosion of the catalyst by fly ashes) [176, Schenk et al. 2009] are significant • At relatively high SO_2/SO_3 levels, the process has to run at a high temperature to prevent formation of ammonium salts • In a 'high-dust' sequence, the fly ashes are loaded with NH_3 • In a 'low-dust' sequence, the reheating of the waste gases is required

Economics

Economics associated with the selective reduction of NO_X are given in Table 3.290.

Table 3.290: Economics associated with the selective reduction of NO$_X$

Type of costs	Costs	
	SNCR	**SCR**
Investment costs (EUR per 1 000 Nm^3/h)	2 500–10 000 ([1])	10 000–83 000 ([1, 2])
Operating costs (EUR per t of NO$_X$ removed)	700–1 200	200 ([3])–5 000 ([1])
Labour (EUR/yr)	20 000 ([1])	20 000 ([1])
Consumables (EUR/t)	150–200 (for NH$_3$ solution) ([1, 4])	NH$_3$ solution ([5]) 11 000 (for catalyst) ([1])
Cost-determining parameters	Consumption of ammonia or urea, abatement target, thermal efficiency, retrofitting ([1])	Use of catalyst and reagents ([1])
Benefits	None, besides benefits from possible NO$_X$ emissions trade ([1])	None, besides benefits from possible NO$_X$ emissions trade

([1]) [176, Schenk et al. 2009].
([2]) 83 000 Nm^3/h for a waste combustion furnace with a capacity of 80 000 tonnes per year [176, Schenk et al. 2009].
([3]) In the case of a large capacity (> 250 000 t/yr) nitric acid production plant [157, ADEME 2004].
([4]) Up to 570 kg NH$_3$ solution per tonne of removed NO$_X$ [176, Schenk et al. 2009].
([5]) 370–450 kg NH$_3$ solution per tonne of removed NO$_X$ [176, Schenk et al. 2009].

A key cost-effectiveness parameter in the case of SNCR is the consumption of ammonia or urea; in the case of SCR, it is the catalyst as well as ammonia or urea. The retrofitting of SNCR is relatively easy because there is no equipment to install other than the injection items and the storage tank for the agent.

Retrofitting of SCR units can require radical modifications of the existing installation and thus demand high investment costs. A revamping of a SCR unit at a nitric acid production plant can cost approximatively EUR 1 240 000 on top of which the cost of the catalyst of approximatively EUR 600 000 should be added [157, ADEME 2004].

Catalyst costs may represent an annualised cost in the range EUR 40 000–80 000 per burner depending on the size of the unit. The use of catalysts involves the payment of licence fees that can represent a total of around EUR 200 000 assuming a catalyst service life of 10 years (or EUR 20 000/yr).

Driving force for implementation
The driving force for using SNCR or SCR is the reduction of NO$_X$ emissions which can affect human health and the environment.

Example plants
SNCR is reported to be used in the chemical industry (e.g. production of ammonia [102, COM 2007]) as well as in other industry sectors such as large combustion plants, waste incineration, cement plants, the metal industry, and greenhouse horticulture [176, Schenk et al. 2009].

SCR is reported to be used in the chemical industry (e.g. production of nitric acid [102, COM 2007]) as well as in other industry sectors such as large combustion plants, waste incineration, the metal industry, and greenhouse horticulture [176, Schenk et al. 2009].

Reference literature
[6, VCI 1995] [11, InfoMil 1999] [92, InfoMil 1999] [102, COM 2007] [136, John Zink 2008] [157, ADEME 2004] [176, Schenk et al. 2009] [178, Yates et al. 2005] [227, CWW TWG 2009] [228, CWW TWG 2011]

3.5.1.5.4 Non-selective catalytic reduction of NO$_X$ (NSCR)

Description
Non-selective catalytic reduction (NSCR) converts the chemicals CO, NO$_X$ and VOCs into CO$_2$, N$_2$ and/or H$_2$O through the use of a catalyst. Although developed as a DeNO$_X$ system, NSCR also considerably reduces the emissions of N$_2$O. Because the non-combusted VOCs are used as the reacting agent this technique requires no extra reagent injections (even if ammonia or urea is also sometimes used). However, the waste gases should not contain more than 0.5 % oxygen (when natural gas is used as a reducing agent for NO$_X$, the acceptable oxygen content can be increased by up to 2 %) [176, Schenk et al. 2009].

The catalyst is often made of platinum and has to be replaced periodically. A lifespan of 2–3 years is generally guaranteed.

A schematic diagram of a non-selective catalytic reduction system is shown in Figure 3.105.


Source: [176, Schenk et al. 2009]
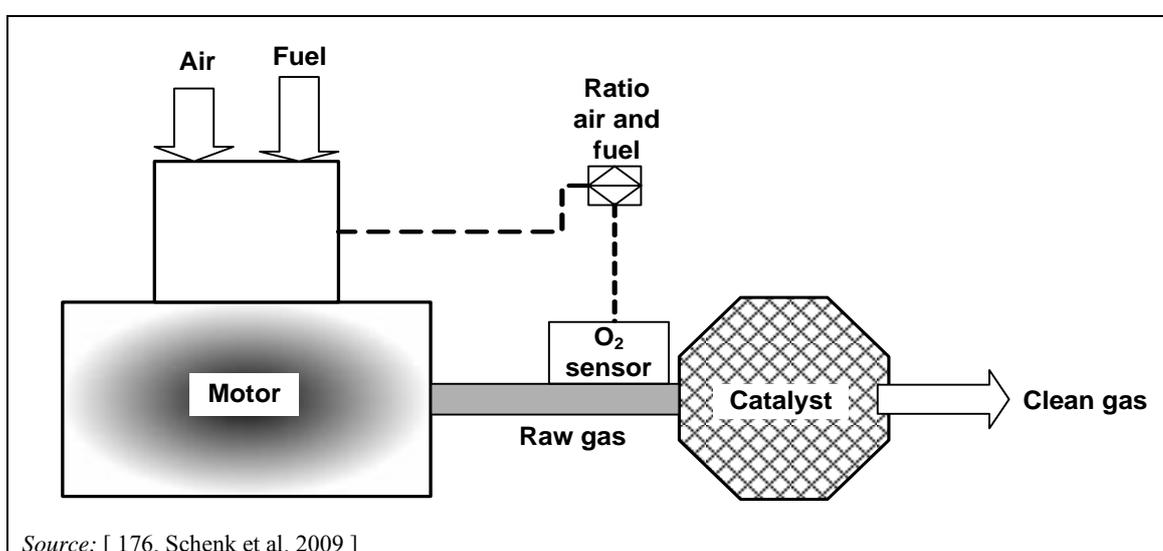
Figure 3.105:   Non-selective catalytic reduction

See also information contained in the LVIC-AAF BREF on the use of NSCR in nitric acid production [102, COM 2007].

Achieved environmental benefits
Abatement efficiencies and emission levels associated with non-selective catalytic reduction are given in Table 3.291.

Table 3.291: Abatement efficiencies and emission levels associated with non-selective catalytic reduction

Pollutant	Abatement efficiency ([1]) (%)	Emission level ([2]) (mg/Nm^3)	Comments
NO$_X$	90–98 ([3])	50 ([3])	—
	NI	200–300 ([4])	Nitric acid production
N$_2$O	> 95 ([4])	< 100 ([4])	Nitric acid production

([1]) Efficiency depends on the specific plant configuration, operational conditions; the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
([2]) The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting [176, Schenk et al. 2009].
([3]) [176, Schenk et al. 2009].
([4]) [102, COM 2007].
NB: NI = no information provided.

Cross-media effects
When hydrocarbon fuels are used, emissions of carbon monoxide (CO), carbon dioxide (CO$_2$) and hydrocarbons (C$_x$H$_y$) will take place. Normally, the carbon monoxide emissions will be less than 1250 mg/m^3, but emissions of hydrocarbons can be up to 5 000 mg/m^3. Emissions of CO$_2$ can be over 12 g/m^3 [102, COM 2007]. At high CO levels, an oxidation catalyst could be placed in series after the catalyst to convert the CO into CO$_2$ [176, Schenk et al. 2009].

Operational data
No information provided.

Applicability
The applicability of the technique is limited.

Application limits and restrictions are given in Table 3.292.

Table 3.292: Application limits and restrictions associated with non-selective catalytic reduction

Issue	Limits/restrictions
Waste gas flow (Nm^3/h)	< 34 000
Temperature (°C)	375–825
Pressure (bar)	< 8
Pressure drop (mbar)	NI
Relative humidity (%)	NI
Dust concentration	NI
Oxygen concentration (%)	0.2–0.7
NO$_X$ concentration (mg/Nm^3)	4 000–8 000
CO concentration (mg/Nm^3)	3 000–6 000
VOC concentration (ppm)	1 000–2 000

NB: NI = no information provided.
Source: [176, Schenk et al. 2009].

Advantages and disadvantages are given in Table 3.293.

Table 3.293: Advantages and disadvantages associated with non-selective catalytic reduction

Advantages	Disadvantages
• No extra reducing agent required	• Limited applicability • Operating temperature may require preheating • Catalyst lifetime of 2–3 years (shorter than for SCR) • Emissions of CO, CO_2 and C_xH_y

Economics
Economics associated with non-selective catalytic reduction are given in Table 3.294.

Table 3.294: Economics associated with non-selective catalytic reduction

Type of costs	Costs	Comments
Investment costs (EUR)	15 000–250 000	Largely dependent on the engine size (80–8 000 horsepower)
Operating costs (EUR)	69 000–244 000	Largely dependent on the engine size (80–8 000 horsepower)
Catalyst	NI	Catalyst has to be replaced periodically. The used catalyst is sometimes sold
Cost-determining parameters	Engine size	
Benefits	None	
NB: NI = no information provided. *Source:* [176, Schenk et al. 2009].		

Driving force for implementation
The driving force for using NSCR is the reduction of NO_X emissions (and sometimes simultaneously N_2O) which can affect human health and the environment.

Example plants
NSCR is reported to be used in the chemical industry (e.g. in the production of nitric acid) as well as in other industry sectors such as the car industry, power generation, and the production of inert gases [176, Schenk et al. 2009].

Reference literature
[102, COM 2007] [176, Schenk et al. 2009]

3.5.1.5.5   Wet gas scrubber for NO_X recovery

Description
NO_X is recovered from waste gases from the reaction, feed tanks, centrifugation and buffers by scrubbing (see Figure 3.106). A general description of the wet scrubbing technique is given in Section 3.5.1.2.4. The first three absorption towers are operated with water, and the last with H_2O_2. H_2O_2 is used to oxidise NO:

$$NO + NO_2 + 2 \, H_2O_2 \rightarrow 2 \, HNO_3 + H_2O$$

$$2 \, NO_2 + H_2O_2 \rightarrow 2 \, HNO_3$$

This drastically improves the absorption efficiency and the emitted NO_X consists of > 98 % NO_2.

Source: [105, COM 2006]
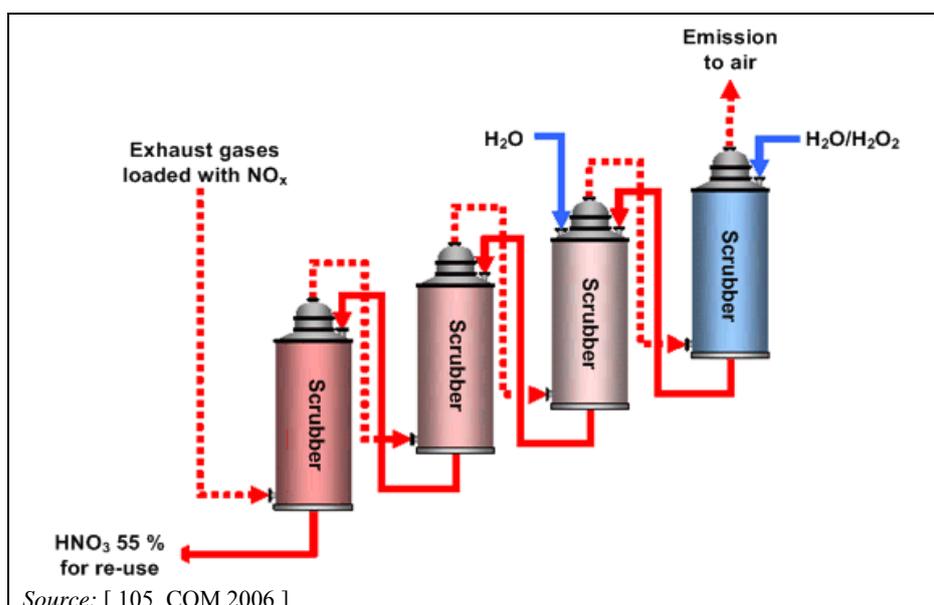
Figure 3.106:   Recovery of NO_X from waste gases with a scrubber cascade

Achieved environmental benefits
The achieved environmental benefits are:

- efficient recovery of NO_X from waste gases;
- emission levels of 113–220 mg/Nm^3 (NO_X measured as NO_2) have been achieved.

Cross-media effects
Energy and H_2O_2 consumption.

Operational data
Operational data of the example:

- volume flow to scrubber cascade: 7 700 m^3/h;
- scrubbing medium in the last scrubber: 15 wt-% H_2O_2.

Applicability
Generally applicable. Especially applicable in cases where even sophisticated scrubbing systems do not achieve comparable emission levels [102, COM 2007].

Economics
Additional costs for H_2O_2, but benefits from the recovery of nitric acid (aqueous solution with < 55 wt-%) for internal use or external sale.

Driving force for implementation
Reduction of NO_X emissions which can affect human health and the environment.

Example plants
Two OFC plants (production of explosives) use this technique for the recovery of NO_X from various waste gases.

Reference literature
[102, COM 2007] [105, COM 2006]

3.5.1.6 Flaring

Description
Flaring is a high-temperature oxidation process used to burn combustible compounds of waste gases from industrial operations. Flares are used for safety reasons or during non-routine operational conditions (e.g. start-ups, shutdowns). Flaring is used to safely combust vented flammable gases (hydrocarbons) at a pressure drop which does not compromise plant relief systems.

At chemical plants, reactors are major sources of flammable gases that may need to be flared, mostly during plant start-ups, shutdowns and emergency situations.

Flaring is also used at installations using anaerobic digesters to produce biogas (e.g. waste water and/or sludge treatment plants, see Sections 3.3.2.3.5.2 and 3.4.2.3). These installations generate a methane-rich biogas that may be used to generate electricity and process heat. The (part of the) biogas that is not consumed or stored is flared [109, COM 2006].

Because flaring is both a source of pollution and leads to the burning of a potentially valuable product, its use should be limited to non-routine or emergency releases. Uncontrolled emissions (especially VOCs) from vents and relief valves should be routed to recovery systems, with flares serving only as a backup system [144, Levy et al. 2006].

Flares can be categorised in several ways, a common one being according to their height as either elevated flares or ground flares.

Elevated flares are the most common type and 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, etc.). Elevated flares are generally designed for large capacities (hundreds of tonnes per hour) and are more suitable to large variations of gas flow.

A typical elevated flare system is shown in Figure 3.107.

Source: [52, US EPA 1995]
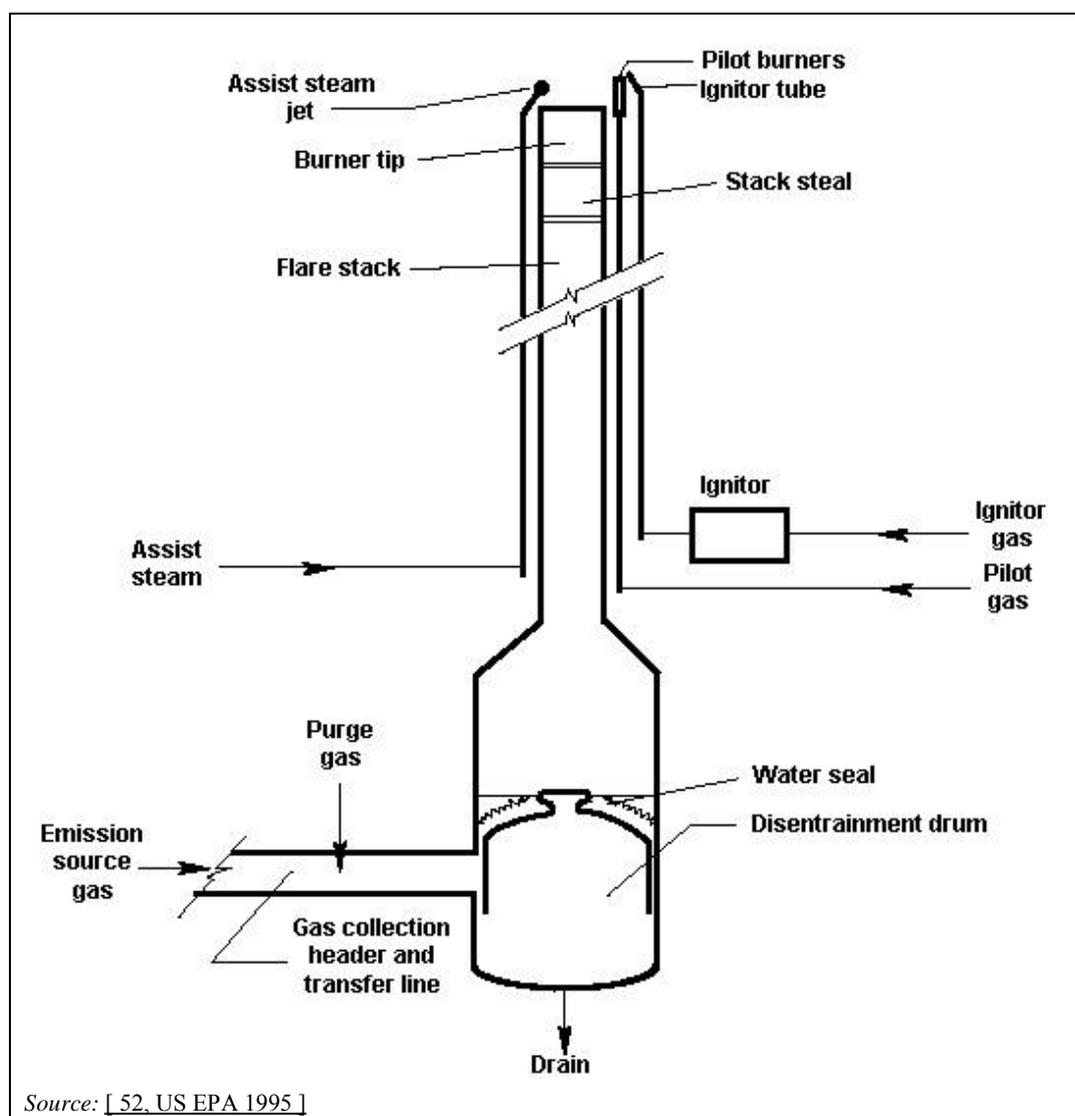
Figure 3.107:   Typical elevated flare system

The elevated flare system consists of [52, US EPA 1995]:

- a gas collection header and piping for collecting gases from processing units;
- a knockout drum (disentrainment drum) to remove and store condensables and entrained liquids;
- a proprietary seal, water seal or purge gas supply to prevent flashback;
- a single or multiple burner unit and a flare stack;
- gas pilots and an ignitor for the mixture of waste gas and air;
- if required, a provision for an 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 (with reduced noise, light and heat nuisance and protection from the wind). 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 mainly includes leaking safety valves and any start-up and shutdown processes.

The large diameter of ground flares provides the possibility for more burners. Thus ground flares 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.

Another classification of flares is made according to the method used for achieving a mixing enhancement at the flare tip in order to attain complete combustion and therefore flare efficiency [142, Akerodolu and Sonibare 2004] and includes the following categories:

- air-assisted flares,
- steam-assisted flares,
- pressure-assisted flares,
- non-assisted flares.

Another type of categorisation depends on the zone in which the oxidation reaction occurs [141, VITO 2009] and includes the following categories:

- flame flares (also called open flame flares),
- chamber flares (also called muffle and screen/shielded flares).

The injector flares and tube flares form the first group of typical flame flares that have no combustion chamber, i.e. an open flame determines the reaction zone. These flares are typically chosen for safety reasons, and are mostly elevated, because of the heat generated by the highly visible flame. The use of these flares is mainly focused on the fast removal of residues through an open flame, and the residence time of the residue flows is less than one second [141, VITO 2009].

The second group of flares is formed by the muffle and screen/shielded flares. These are, in fact, thermal oxidisers and more information can be found in Section 3.5.1.3.5. The reason is that through their physical construction, the reaction zone is, in fact, a (semi-open) combustion chamber, consisting of a shielded area, with or without a controlled air supply (screen or muffle). The reaction takes place in a more controlled way so that higher efficiencies are obtained. Typically, the residence time exceeds one second, and a high temperature is guaranteed through the specific construction of the chamber and the supplies for waste gas streams and utilities. This type of technique can be found for both elevated or for lower-level (ground) versions of flares [141, VITO 2009].

Complete combustion with flare systems requires sufficient combustion air and a proper mixing of air and waste gas. Smoking may result from combustion, depending upon waste gas composition and the quantity and distribution of combustion air. Waste gases which contain methane, hydrogen, carbon monoxide and ammonia usually burn without smoke. Waste gases which contain heavy hydrocarbons (i.e. carbon to hydrogen mole ratio greater than 0.35) such as alkanes with more than one carbon atom, olefins and aromatics, have a greater tendency to smoke and require better mixing for smokeless flaring [142, Akerodolu and Sonibare 2004]. Industry usually requires a smokeless capacity of 10–15 % for elevated flares and of 100 % for ground flares. An external momentum force is used as a 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 8–11 MJ/Nm^3 for complete combustion, otherwise auxiliary fuel must be added. In some cases, even flaring waste gases with the necessary heat content will require supplemental heat. [238, Freund 2010]

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 3.108, Figure 3.109 and Figure 3.110.

Source: [9, BASF 1999]
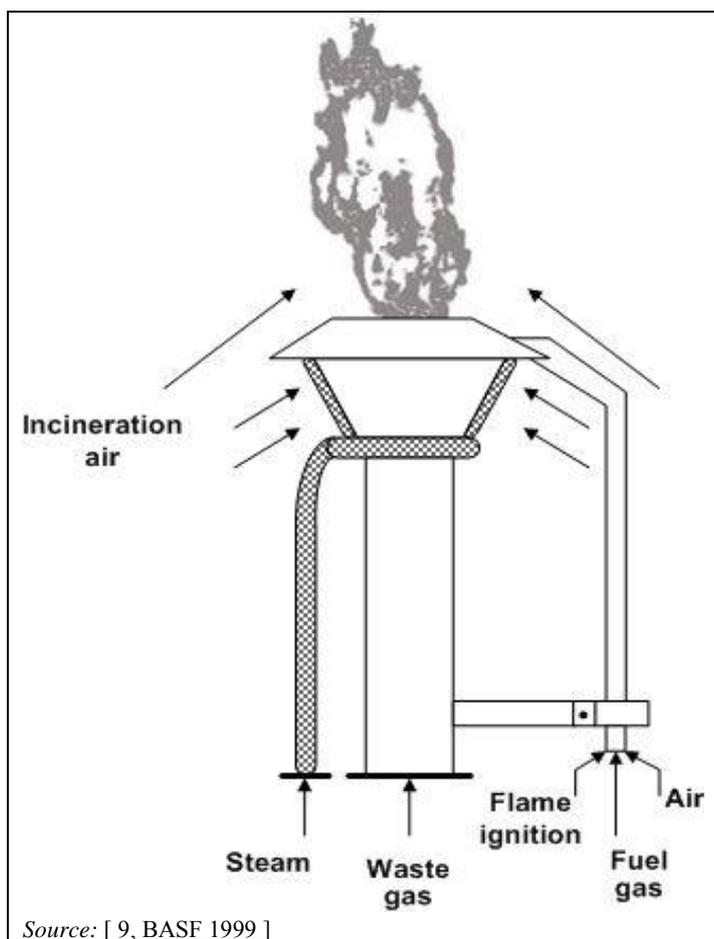
**Figure 3.108:** **Injector rod flare**
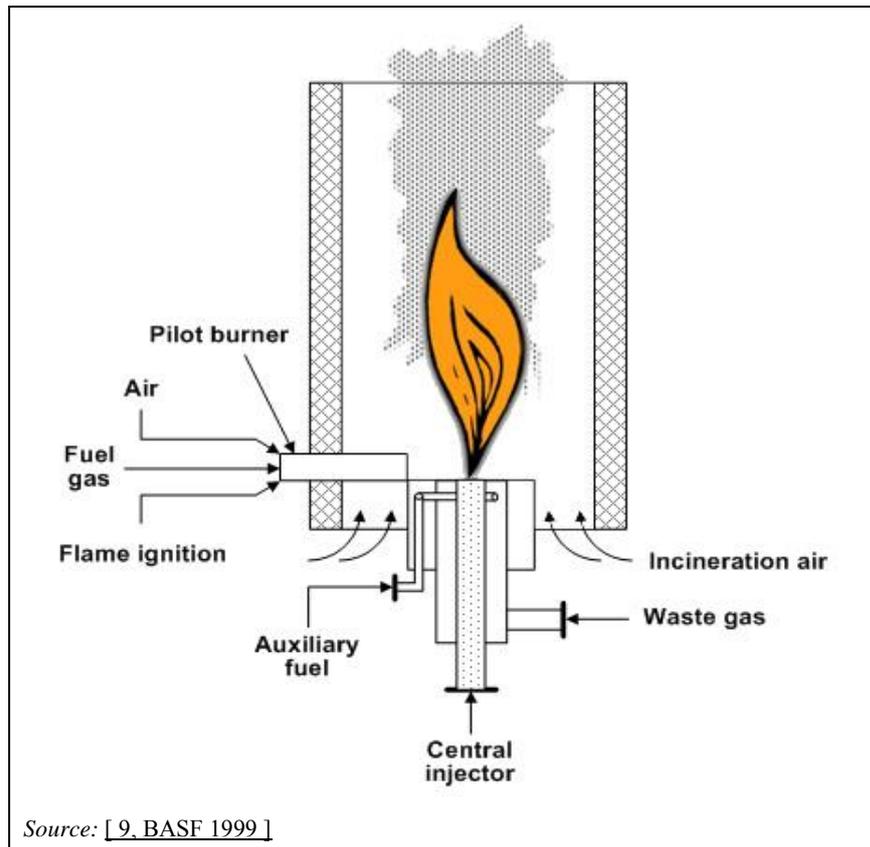
Figure 3.109: Shielded flare
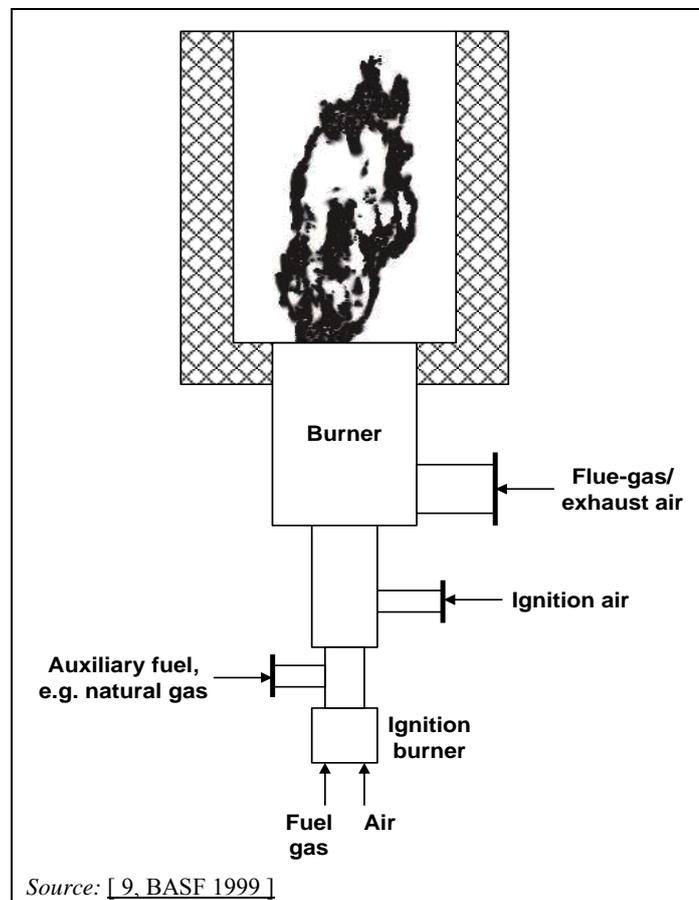
Figure 3.110: Muffle flare

Achieved environmental benefits

Abatement efficiencies and emission levels associated with flaring are given in Table 3.295.

Table 3.295: Abatement efficiencies and emission levels associated with flaring

Pollutant	Elevated flare		Ground flare	
	Abatement efficiency [1] (%)	Emission level [2] (mg/Nm³)	Abatement efficiency [1] (%)	Emission level [2] (mg/Nm³)
VOCs (including CH₄)	> 98 [3, 4, 5]	NI	> 99 [3, 5]	NI
NO_X	NI	400 (200 ppm)	NI	400 (200 ppm)
	NI	108 [6]	NI	108 [6]
CO	NI	588 [6]	NI	588 [6]

[1] Efficiency depends on the specific plant configuration and operational conditions; the performances indicated are based upon half-hourly averages [176, Schenk et al. 2009].
[2] The emission levels reported are indicative of what is being achieved at some industrial installations under normal operating conditions; because emission levels strongly depend on the specific plant configuration and operating conditions, the values given should be used with extreme caution for permitting.
[3] Under optimum conditions, i.e. heat content of waste gas > 8–11 MJ/Nm³; low flows and low heat content achieve lower combustion efficiencies (as low as 65 %) [142, Akerodolu and Sonibare 2004].
[4] [52, US EPA 1995] [142, Akerodolu and Sonibare 2004].
[5] [24, InfoMil 2000].
[6] [52, US EPA 1995].
NB: NI = no information provided.

The achievable emission levels mentioned in Table 3.295 report the destruction of air pollutants (VOCs) by flaring. The other parameters (NO_X) refer to emissions caused by flaring. Flaring has no waste gas treatment installed, hence pollutants generated by the incineration of waste gases which contain sulphur and/or halogens, NO_X, carbon monoxide, soot, etc. are normally not controlled. For these reasons, ground flares are not suited for toxic gases. The combination/recombination reaction to form dioxins, however, is not favoured because of the lack of a 'recombination window' and metal surfaces acting as catalysts.

The abatement performance of flaring, as described in the table above, will be > 98 % if the flare is designed and operated properly [24, InfoMil 2000] [52, US EPA 1995] [176, Schenk et al. 2009]. Important parameters for achieving the optimum combustion efficiency are described below under operational data. The performance range under non-optimum conditions may be well below 98 % [24, InfoMil 2000] [142, Akerodolu and Sonibare 2004].

Cross-media effects

Flare emissions will include, at minimum, nitrogen oxides (NO_X), carbon monoxide (CO), and uncombusted flared gas compounds (e.g. VOCs). In addition, if the flared gas contains sulphur-bearing compounds, emissions will also include hydrogen sulphide (H_2S) and sulphur dioxide (SO_2) [169, TCEQ 2016], thus causing potential odour nuisances (mainly for ground flares).

The main utilities and consumables include:

- 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 overpressure;
- pilot gas;
- energy.

A typical pressure drop is 1 kPa [9, BASF 1999].

Flaring can cause noise emissions. The most significant noise sources are [34, HMIP 1993]:

- smoke suppressant injection;
- combustion processes;
- 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 the 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 is thus an important design aspect that needs to be addressed for new flares. Noise avoidance aspects include:

- reduction or attenuation of the high-frequency steam jet noise by using multiport steam injectors, which can also lead to increased coke formation under low flow conditions; orifice design to cope with this drawback is essential;
- installing the injectors in a way that the jet streams can interact and reduce the mixing noise;
- increasing the efficiency of the suppressant with better and more responsive forms of control;
- restricting the 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 include:

- light nuisance from elevated flares;
- odour nuisance because of insufficient combustion (mostly with ground flares).

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, BARPI). The results can be found in the ARIA database managed by that organisation [249, BARPI 2016].

Operational data
Combustion efficiency is one of the key parameters used for controlling flares. The combustion efficiency of the flare determines what fraction of the flared gas remains uncombusted. The uncombusted flared gas compounds are generally volatile organic compounds, but may also include H_2S, CO, ammonia, and other organic and inorganic compounds present in the flared gas [169, TCEQ 2016]. The combustion of hydrocarbons at a flare tip cannot be 100 % efficient (around 98 % to 99 % at best), but there are great difficulties for determining the level of unburnt hydrocarbons. The use of different measurement and reporting methodologies can lead to very different apparent emission levels for similar activities.

The operating variables that can be monitored to maximise combustion efficiency include [144, Levy et al. 2006]:

- the ratio of fuel gas to assist gas (air or steam) and burner tip velocity;
- the heat content of the flare fuel mixture.

Monitoring [34, HMIP 1993]:
The flow rate of the smoke suppressant to the flare tip should be checked to ensure that sufficient suppressant is introduced, but not more than is required to prevent smoking. This can be achieved in four different ways:

- by an array of thermocouples rated for a temperature of at least 1 000 °C;
- by a ground-based infrared detector;
- by monitoring the ratio of assist-gas rate to flare gas rate, and maintaining this ratio within the appropriate range;
- by visual monitoring (remote TV camera).

A more stringent monitoring policy is required for ground flares because of health and safety risks.

A rapid response of the control system is essential, preferably by means of an electronic transmission of control signals between the usually remote flare stack and the relevant control room. Installation of a TV to monitor the flare in the control room should be considered to allow a manual intervention of suppressant control if necessary.

For the pilot ignition system of the flare, the operational monitoring equipment could include some of the following tools:

- thermocouples (but looking out for erroneous signals);
- direct surveillance of the pilot flame (e.g. TV surveillance);
- infrared monitoring, sometimes modified with optical monitoring to surmount the absorption of infrared radiation by water;
- luminosity measurement;
- UV monitoring;
- ionisation probes;
- low-pressure alarm;
- flow control of the purge gas.

A device is required for the continuous detection of the presence of the pilot flame.

The operating temperature of a flare depends upon the material to be combusted. A temperature that is too high may cause refractory insulation damage as well as the production of excess NO_X, while a temperature that is too low may result in the production of excess carbon monoxide and unburnt hydrocarbons. High and low temperature alarms for the flare stack should be provided as well as a high-high interlock to shutdown the gas supply to the flare stack in the event of an excessively high temperature [143, US Army 2008].

Applicability
Flares are widely used in the oil, gas and petrochemical industries to safely dispose of surplus combustible gases and vapours when there is no opportunity to reuse or recycle them. VOCs 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. However, flares are normally not used as a continuous measure. They can also be used to burn waste gases generated by sewerage/sludge digesters.

Whereas elevated flares are normally used as emergency and relief gas flaring, ground flares are more often employed for 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 occur, a combination with an elevated flare is required.

Application limits and restrictions are given in Table 3.296.

Table 3.296: Application limits and restrictions associated with flaring

Issue	Limits/restrictions
Typical gas flows	0–1 800 000 Nm^3/h ([1]) (upper limit for elevated flares)
Minimum calorific value of incoming waste gas (MJ/Nm^3)	8–11 ([2])
Combustion temperature (°C)	> 800 ([3])
Pressure	Atmospheric ([2])
Oxygen content after incineration	> 5 % ([4]) (muffle flare)
Flare velocity (m/s)	0–20 ([4]) (to prevent flashback)
([1]) [52, US EPA 1995]. ([2]) [176, Schenk et al. 2009]. ([3]) [250, Ullmann's 2011]. ([4]) [9, BASF 1999].	

Advantages and disadvantages are given in Table 3.297.

Table 3.297: Advantages and disadvantages associated with flaring

Advantages	Disadvantages
General • Economical way of processing accidentally and incidentally large quantities of VOCs that are contained in wastes gases • 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 • May cause noise, smoke, heat and light nuisance (smoke suppressants needed) • Heat of combustion not recoverable • Not suitable for the treatment of halogenated compounds • High costs for retrofitting
Elevated flares • Quick and safe release of large amounts of waste gas • Standby equipment for emergency use	Elevated flares • Flame flares cause light and 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, requires a combination with elevated flares • Increased health and safety risks when malfunctioning • Potentially reduced efficiency due to poor fuel quality • Odour nuisance

Economics
Economics associated with flaring are given in Table 3.298.

Table 3.298: Economics associated with flaring

Type of costs	Elevated flare	Ground flare
Investment costs (EUR per 1 000 Nm^3/h)	~ 100 000–650 000 (^{1})	Could cost three to four times as much as elevated flares (^{2})
Operating costs (per 1 000 Nm^3/h)	NI	NI
Labour	Can also vary widely; the skill of the maintenance personnel is the essential factor here	
Cost-effectiveness (per tonne of pollutant controlled per year)	NI	NI
Cost-determining parameters	Potential additional fuel	
Benefits	None	

(^{1}) Onshore design without landing. The costs can vary widely because they are dependent on the number of hours the flare is used. Because a flare is primarily a safety system, the number of hours it is used will be low (10 to 100 hours per year) [176, Schenk et al. 2009].
(^{2}) [142, Akerodolu and Sonibare 2004].
NB: NI = no information provided.

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 h/yr and 100 h/yr. Flares at the lower end of the investment and operating cost ranges have a higher flow capacity (approximately 300 000 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 a 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. The cost per tonne of pollutant controlled largely depends upon the annual hours of operation. Infrequent use of the flare will result in greater costs per tonne of pollutant controlled, while more frequent use means lower costs per tonne of pollutant controlled.

Driving force for implementation
The main driving force for implementation is safety.

Example plants
Flares are used notably in many refineries, and petrochemical and polymer production plants around the world. Flares are also reported to be used in the iron and steel sector as well as at landfill facilities and waste water treatment plants (e.g. to treat excessive biogas).

Reference literature
[9, BASF 1999] [24, InfoMil 2000] [34, HMIP 1993] [52, US EPA 1995] [80, World Oil Magazine 2000] [106, COM 2007] [109, COM 2006] [141, VITO 2009] [142, Akerodolu and Sonibare 2004] [143, US Army 2008] [144, Levy et al. 2006] [169, TCEQ 2016] [176, Schenk et al. 2009] [179, UBA DE 2009] [247, COM 2003] [249, BARPI 2016] [250, Ullmann's 2011]

3.5.2 Combination of waste gas treatment techniques: Central waste gas incineration

Description
Waste gas streams from various (chemical) installations are treated in a central incinerator/oxidiser. In many cases a combination of treatment techniques is applied in order to reach the desired emission levels. The waste gas streams may need to be pretreated (e.g. dedusting) before entering the incinerator/oxidiser. Similarly, depending on the pollutants contained in the flue-gas after incineration, further treatment might be needed (e.g. desulphurisation).

Examples of combining incineration with other waste gas treatment techniques are provided in Table 3.299 below.

Achieved environmental benefits
See Table 3.299 and Section 3.5.1 for the individual treatment techniques.

Cross-media effects
See Table 3.299 and Section 3.5.1 for the individual treatment techniques.

Operational data
Operational data for combined waste gas treatment techniques are given in Table 3.299.

Table 3.299: Combined waste gas treatment techniques

Plant 1 [185, UBA DE 2009]	Plant 2 [186, UBA DE 2009]	Plant 3 [187, UBA DE 2009]	Plant 4 [188, UBA DE 2009]
Description			
Organic waste gases originating from four installations are incinerated at 850 °C. After cooling of the waste gas, the inorganic pollutants are washed out in a jet scrubber. The treated waste gas is emitted via a stack.	Organic waste gases originating from four installations are incinerated in a vertical combustion chamber at temperatures of at least 850 °C. After cooling of the waste gas, the inorganic pollutants are washed out in a multi-stage flue-gas scrubbing system downstream. For removal of silica dust, this is followed by wet absorption with subsequent ionisation scrubbing. Sodium bisulphite is added in solution to eliminate possible chlorine emissions. The treated waste gas is emitted via a stack.	Organic waste gases are incinerated above 900 °C. After cooling of the waste gas, the inorganic pollutants are washed out in a two-stage flue-gas scrubbing system. Given relevant raw gas flows, NO_X is removed in the combustion by SNCR using ammonia. The treated waste gas is emitted via a stack.	Waste gas flows loaded with nitrogen oxides and organic compounds are incinerated at two series-connected combustion chambers: CC21 (reduction) and CC22 (oxidation). After treating and cooling, the waste gas is emitted via a stack. The heat resulting from the incineration is used for the production of steam (30 to 40 bar).
Emission abatement system			
1. Thermal oxidation With natural gas and liquid substitute fuel (methanol), T in reaction chamber is 850–1 200 °C (850 °C in operation), residence time of 1 second in the reaction chamber.	*1. Thermal oxidation* With natural gas (fuel throughput approximately 360 m³/h, at least 40 m³/h), T in reaction chamber is 850 °C, residence time of 1 second in the reaction chamber.	*1. Thermal oxidation* With natural gas and liquid substitute fuels, T in reaction chamber is 850–980 °C, residence time of 1 second in the reaction chamber.	*1. Thermal oxidation* With natural gas, T in reaction chamber CC21 is 1 350 °C and in CC22 is 900 °C, residence time in reaction chamber CC21 is 0.7 s and in CC22 is 1.8 s.
2. Two-stage wet gas scrubber Jet gas scrubber (NaOH solution/water) and packed column (1.5 m, NaOH solution/water, 50 °C, pH 8).	*2. Wet scrubber* Water (80–120 m³/h, at 25–35 °C), pH becomes acidic due to SO_X and HCl from flue-gases (pH kept at 5 by addition of NaOH).	*2. Two-stage wet gas scrubber* NaOH solution/water (at 50–60 °C, first stage pH 2–6, 2nd stage pH 7.5–9), pH in first stage becomes acidic due to SO_X and HCl from flue-gases.	
	3. Ionisation wet ESP	*3. SNCR* Reduction with ammonia, ammoniacal liquor (25 %)	
Cross-media effects			
The inorganic waste water generated during jet gas scrubbing is directly discharged to the river and the organic waste water is discharged to a WWTP.	The waste water generated during wet gas scrubbing (max. 15 m³/h; HCl approximately 30 000 mg/l, SiO_2 approximately 3 300 mg/l, COD< 1 mg/l and AOX< 1 mg/l) is discharged to a WWTP.	The inorganic waste water generated during waste gas treatment (7 m³/h; chloride: 140 kg/m³, sulphate: 60 kg/m³) is discharged to a WWTP and the organic waste water is returned to the combustion chamber of the thermal oxidation unit to be incinerated.	The blowdown water of the steam drum is channelled to the central WWTP along with other waste waters.

Plant 1 [185, UBA DE 2009]	Plant 2 [186, UBA DE 2009]	Plant 3 [187, UBA DE 2009]	Plant 4 [188, UBA DE 2009]
Consumables			
NaOH solution (waste gas scrubber): 35 m^3/h, *Air:* 0–10 000 kg/h, *Process water*: 11 kg/h, *Boiler feed water*: 6.6 kg/h, *Natural gas*: 600 kg/h, *Steam*: 4 400 t/month	*NaOH solution (waste gas scrubber):* 0–100 kg/h *Combustion air:* 1 500–7 500 Nm^3/h, *Process water*: 45 000 kg/h, *Boiler feed water*: 60 Nm^3/h, *Natural gas*: 50–250 Nm^3/h, *Steam (50 bar)*: 10 kg/h, *Nitrogen:* 0–700 Nm^3/h, *Compressed air:* 15 Nm^3/h, *Air:* 10 Nm^3/h, *Sodium bisulphite solution:* 0–5 kg/h	*NaOH solution (waste gas scrubber):* no data *Combustion air:* 2 000–4 000 Nm^3/h, *Process water*: 7 Nm^3/h, *Boiler feed water*: 3 Nm^3/h, *Natural gas*: 30–150 Nm^3/h, *Steam (50 bar)*: 3 t/h, *Liquid support fuel:* 0–120 kg/h, *Ammoniacal liquor (25 %):* max. 50 l/h	*Air:* 0–10 000 kg/h *Ammonia water:* 50 kg/h *Boiler feed water:* 6 000 kg/h *Natural gas:* 200 kg/h *Steam:* 4 400 t/month
Raw gas characteristics before the abatement system			
TOC > 7 000 mg/Nm^3 at > 99 % removal efficiency HCl > 10 000 mg/Nm^3 at > 98 % removal efficiency SO$_2$ > 800 mg/Nm^3 at > 85 % removal efficiency	TOC ~ 28 000 mg/Nm^3 at > 99.5 % removal efficiency HCl ~ 25 000 mg/Nm^3 at > 99.5 % removal efficiency (max. proportion after incineration before scrubbing) SiO$_2$ dust ~ 4 000 mg/Nm^3 at > 98 % removal efficiency (max. proportion after incineration before scrubbing)	TOC > 5 000 mg/Nm^3 at > 99.5 % removal efficiency (max. of 5 wt-%) HCl > 10 000 mg/Nm^3 at > 98 % removal efficiency (max. of 1 wt-%) NO$_X$ > 800 mg/Nm^3 at > 98 % removal efficiency (max. of 0.1 wt-%) SO$_2$ max. of 2 wt-% Chlorine max. of 0.5 wt-% HF max. of 0.01 wt-% HBr max. of 0.01 wt-% Hydrogen max. of 50 wt-%	TOC ~ 10 000 mg/Nm^3 at > 99 % removal efficiency NO$_X$ (as NO$_2$) ~ 90 000 mg/Nm^3 at > 99 % removal efficiency SO$_2$ present in traces.
Emissions at the stack			
Measured in 2008	Measured in 2008	Measured in 2008	Measured in 2007
Flow: 15 200 m^3/h	Flow: 8 615 m^3/h	Flow: 4 000 m^3/h	Main gas flow: 6 850 m^3/h
Waste gas T: 270 °C	Waste gas T: 34 °C (moisture content of waste gas: 100 %)	Waste gas T: 52 °C (moisture content of waste gas: 100 %)	Waste gas T: 252 °C
O$_2$ content: 12.71 vol-% (mean value from 48 half-hourly averages, min. value of 11.96 vol-%, max. of 13.3 vol-%) Reference O$_2$ content: No need to standardise emissions.	O$_2$ content: 15 vol-% (mean value from 37 half-hourly averages with a min. value of 14.75 vol-% and a max. of 16.73 vol-%) Reference O$_2$ content: 10 %	O$_2$ content: 12.79 vol-% (mean value from 48 half-hourly averages, min. value of 11.77 vol-%, max of 19.04 vol-%) Reference O$_2$ content: No need to standardise emissions.	O$_2$ content: 8.7 vol-% (mean value from 3 half-hourly averages, min. value of 8.6 vol-%, max. of 8.8 vol-%) Reference O$_2$ content: No need to standardise emissions.
Mean values from 48 half-hourly averages from continuous emission measurement: **TOC:** 0.5 mg/Nm^3 with 0.008 kg/h (max. 1 mg/Nm^3)	Mean values from 37 half-hourly averages from continuous emission measurement: **TOC:** 25 mg/Nm^3 with 0.21 kg/h (min. 13 mg/Nm^3, max. 48 mg/Nm^3)	Mean values from 86 half-hourly averages from continuous emission measurement: **TOC:** 2 mg/Nm^3 with 0.008 kg/h (min. < 1 mg/Nm^3, max. 32 mg/Nm^3)	**TOC:** every single substance < limit of detection (0.1 mg/Nm^3) Mean value from 3 half-hourly averages: **NO$_X$:** 156 mg/Nm3 (min. 130 mg/Nm^3,

Plant 1 [185, UBA DE 2009]	Plant 2 [186, UBA DE 2009]	Plant 3 [187, UBA DE 2009]	Plant 4 [188, UBA DE 2009]
NO$_X$: 151 mg/Nm^3 with 2.3 kg/h (min. 82 mg/Nm^3, max. 256 mg/Nm^3) **HCl:** 12 mg/Nm^3 with 0.18 kg/h (min. 0.5 mg/Nm^3, max. 29 mg/Nm^3) **SO$_2$:** 3 mg/Nm^3 with 0.05 kg/h (min. 1 mg/Nm^3, max. 6 mg/Nm^3) **CO:** 11 mg/Nm^3 with 0.17 kg/h (min. < 5 mg/Nm^3, max. 19 mg/Nm^3) **CO$_2$:** 98 162 mg/Nm^3 with 1 492 kg/h (min. 89 951 mg/Nm^3, max. 125 159 mg/Nm^3)	**NO$_X$:** 12 mg/Nm^3 with 0.1 kg/h (min. 8 mg/Nm^3, max. 18 mg/Nm^3) **HCl:** 27 mg/Nm^3 with 0.23 kg/h (min. 18 mg/Nm^3, max. 36 mg/Nm^3) **SO$_2$:** 207 mg/Nm^3 with 1.78 kg/h (min. 112 mg/Nm^3, max. 332 mg/Nm^3) **CO:** 615 mg/Nm^3 with 5.3 kg/h (min. 199 mg/Nm^3, max. 878 mg/Nm^3) **CO$_2$:** 108 071 mg/Nm^3 with 931 kg/h (min. 104 492 mg/Nm^3, max. 112 236 mg/Nm^3) **Cl$_2$:** < 2 mg/Nm^3 with < 0.02 kg/h (min. < 2 mg/Nm^3, max. < 2 mg/Nm^3)	**HCl:** 14 mg/Nm^3 with 0.06 kg/h (min. < 1 mg/Nm^3, max. 55 mg/Nm^3) **SO$_2$:** < 1 mg/Nm^3 with < 0.002 kg/h (min. < 1 mg/Nm^3, max. 1 mg/Nm^3) Mean values from 36 half-hourly averages from continuous emission measurement: **NO$_X$:** 107 mg/Nm^3 with 0.42 kg/h (min. 43 mg/Nm^3, max. 281 mg/Nm^3)	max. 174 mg/Nm^3) **SO$_2$:** < 1 mg/Nm^3, below limit of detection (min. < 1 mg/Nm^3, max. < 1 mg/Nm^3) **CO:** 5.8 mg/Nm^3 (min. 5.6 mg/Nm^3, max. 5.9 mg/Nm^3) **CO$_2$:** 5.5 vol-% (min. 5.4 vol-%, max. 5.5 vol-%)
Mean value from 12 individual samples taken over 24 hours: **N$_2$O:** 22 mg/Nm^3 with 0.33 kg/h (min. 10 mg/Nm^3, max. 49 mg/Nm^3).	Mean value from 9 individual samples taken over 20 hours: **N$_2$O:** < 2 mg/Nm^3 with < 0.02 kg/h (min. < 2 mg/Nm^3, max. < 2 mg/Nm^3). **Dust (SiO$_2$) (4 measurements):** < 1 mg/Nm^3 with < 0.01 kg/h	Mean values from 61 half-hourly averages from continuous emission measurement: **CO:** 16 mg/Nm^3 with 0.06 kg/h (min. < 5 mg/Nm^3, max. 59 mg/Nm^3) **CO$_2$:** 93 652 mg/Nm^3 with 374 kg/h (min. 45 630 mg/Nm^3, max. 118 102 mg/Nm^3) Mean value from 12 individual samples taken over 48 hours: **N$_2$O:** 424 mg/Nm^3 with 1.7 kg/h (min. 79 mg/Nm^3, max. 1 650 mg/Nm^3) **Ammonia:** < 5 mg/Nm^3 with < 0.02 kg/h (min. < 5 mg/Nm^3, max. < 5 mg/Nm^3)	Calculated alternatively with emission factors: **N$_2$O:** 2.15 mg/Nm^3 with 0.01 kg/h, below limit of detection.
Economics			
Investment costs of approximately EUR 2.5 million. Annual operating and maintenance costs are not specified.	Investment costs of approximately EUR 6 million. Annual operating and maintenance costs are not specified.	Not specified.	Investment costs: EUR 6.6 million Maintenance costs: EUR 200 000 per year (including servicing) Annual operating costs: EUR 1.6 million (including waste water) Servicing: Part of the maintenance costs (waste water)

Applicability
See Section 3.5.1 for the individual treatment techniques.

Economics
See Table 3.299 and Section 3.5.1 for the individual treatment techniques.

Driving force for implementation
See Section 3.5.1 for the individual treatment techniques.

Example plants
Central waste gas treatment plants in Germany (see Table 3.299). Aluchemie (NL) applies a recuperative thermal oxidation with pre- and post-treatment for the treatment of waste gases.

Reference literature
[185, UBA DE 2009] [186, UBA DE 2009] [187, UBA DE 2009] [188, UBA DE 2009]

3.5.3 Combination of waste water and waste gas treatment techniques: Incineration chambers

Description
Incineration chambers are a type of incinerator/oxidiser designed specifically for the combined incineration of liquid waste and waste gases, as well as solids dispersed in liquids, and are used in the chemical industry for the incineration of liquids and process off-gas. More information can be found in the Waste Incineration BREF [108, COM 2006].

Achieved environmental benefits
Reduction of emissions to air and water.

Cross-media effects
Consumption of energy and materials to run the installation.

Operational data
An incineration facility with a burning chamber, a heat recovery system (5.3 MW steam boiler heat recovery), a recirculation system, acid and caustic washing units and SCR for the incineration of waste gases from a multi-purpose plant producing pharmaceutical chemicals and active pharmaceutical ingredients can achieve the emission values given in Table 3.300 over a year (reference O_2: 10 %) with a residual off-gas flow rate of 12 500 Nm^3/h [227, CWW TWG 2009].

Table 3.300: Example of environmental performance of an incineration facility

Parameters	Emission value (mg/Nm^3)	Comments
NH_3	1.1	Single measurement
NO_X (as NO_2)	22	Continuous measurement
HF	0.13	Single measurement
PCDDs/PCDFs	0.01 ng/Nm^3	Single measurement
HCl	1	Continuous measurement
Br (as HBr)	0.8	Single measurement
Dust	5	Single measurement
TOC (as C)	0.56	Continuous measurement
SO_2	1.9	Single measurement
CO	20	Continuous measurement
Source: [227, CWW TWG 2009].		

More examples of environmental performance figures of incineration facilities can be found in the Waste Incineration BREF [108, COM 2006].

Applicability
Depends on the overall waste and emission treatment concept.

Economics
No information provided.

Driving force for implementation
Driving forces for implementation include complying with legislation.

Example plants
Various example plants are mentioned in the Waste Incineration BREF [108, COM 2006].

Reference literature
[108, COM 2006] [227, CWW TWG 2009]

3.5.4 Techniques to prevent/reduce diffuse VOC emissions

3.5.4.1 Overview

Diffuse VOC emissions are non-channelled emissions that are not released via specific emission points such as stacks. Diffuse emissions of VOCs within the chemical/petrochemical sector can result from:

- 'area' sources such as open storage areas/tanks, open pan filters or waste water treatment facilities, or
- 'point' sources such as pressurised components on a process plant (e.g. pipe flanges and valves).

Diffuse emissions from point sources are referred to as **fugitive emissions**. Fugitive emissions are characterised as largely random occurrences, and typically occur through the relaxation or progressive wear and tear of sealing elements of particular equipment (e.g. pumps, flanges, valves, tank lids, compressors, agitators, and mixers); in the case of poor construction/installation, operation, maintenance or design; or through the failure of equipment.

Whilst the quantity of fugitive emissions is usually small for a single component (except in case of catastrophic failure), the large number of components in a large-scale processing plant (e.g. LVOC) results in aggregate fugitive emissions that might be significant.

Diffuse VOC emissions are of concern in the chemical industry, mainly in the production of organic compounds. Some VOCs are classified as toxic (e.g. benzene, vinyl chloride monomer, ethylene dichloride). In addition, VOCs are one of the major contributors (along with NO_X and CO under sunny conditions) to the formation of tropospheric ozone, which can be harmful to health. Some VOCs can also be highly odorous (e.g. aldehydes, amines, mercaptans and other sulphur-containing compounds), and these can become a nuisance to the population living near an installation, even at very low concentrations. Some VOCs are also a problem as a result of their ozone depletion and/or global warming potential.

Techniques to reduce diffuse emissions can be implemented during:

- process and plant design;
- plant installation and commissioning;
- plant operation.

Table 3.301 gives an overview of diffuse and channelled VOC emissions from the chemical sector.

More specific information on techniques to reduce diffuse VOC emissions from storage tanks can be found in the Emissions from Storage (EFS) BREF [113, COM 2006].

Table 3.301: Overview of diffuse and channelled VOC emissions from the chemical sector

Type of emissions source	Description	Relative contribution to total plant VOC emissions	Quantification of emissions	Control of emissions	Comments
Atmospheric vents	Emissions from process vents. These include process emissions and purging emissions if these discharge to atmosphere, whether or not the discharge is through an abatement device. Excluded: tank vent emissions, loading vent emissions, emissions resulting from opening of process vessels, whether resulting from operations or from maintenance activities.	Low for most processes. Can be more significant in OFC plants (intermitted vents not always fit for abatement). Can be high contributors in polymer plants as a result of degassing of finished product.	Calculations based on process data. Calculations can be complemented by flow and concentration measurements, if needed; need to ensure that emissions at the time of measurement are representative.	Modify process conditions. Polymer vents: enhance separation of unreacted monomers. Connect to emission abatement device.	Cost of retrofitting of abatement device can be high for small vents or for large vents with low VOC concentration, therefore thresholds need to be defined below which abatement is not economically justified.
Safety valves (SV)	Emissions resulting from the opening of safety valves to the atmosphere caused by excessive pressure in the protected equipment. Internal leak of SV is considered part of the fugitive emissions.	Low: related to incidents.	Detection of release and calculation based on SV release model to calculate emissions from SV opening events.	Avoid incidents. Blowdown system.	Connection of SV to an existing flare entails very high costs if it requires upgrading of the flare collection. It is not justified for SV releasing small quantities in the event of incidents.
Opening of vessels and tanks	Emissions resulting from opening of process vessels, whether resulting from operations (e.g. batch OFC process) or from maintenance activities (e.g. cleaning, inspection).	Low contribution for most processes, can be higher for some OFC processes. Needs to be taken into account for storage tanks.	Estimate the emission in advance during the preparation of the procedure.	Deeper depressurisation and enhanced flushing before opening.	Capture and abatement of emissions is generally not feasible.
Tank venting	Emissions from atmospheric storage tanks, including vents from cone roof tanks and pressure vacuum vent (PVV) from tanks with nitrogen blanketing. Excluded: emissions from pressurised vessels and tanks cleaning emissions.	Depends on the nature and quantity of liquids stored in atmospheric tanks. Tank emissions can be a significant source for large LVOC plants.	Calculation of emissions per API/EPA method (TANKS programme) is accurate for well-maintained tanks. It is therefore useful to complement this with a programme of seal quality checking.	See Reference Document on Emissions from Storage [113, COM 2006]. Appropriate controls for each service are defined.	Spot measurements cannot be used to calculate emissions over a long duration (e.g. a year) because of variability according to type of operations and weather conditions.

Type of emissions source	Description	Relative contribution to total plant VOC emissions	Quantification of emissions	Control of emissions	Comments
Loading	Emissions resulting from loading of ships, barges, trucks, railcars or other mobile containers, whether fitted with vapour abatement device or not.	Loading of volatile substances can contribute considerably if no abatement or recovery of the volatile material is done.	Emission factors per loading are available based on the evolution of the concentration in the displaced vapours. These methods are accurate.	Vapour return, vapour recovery or abatement for loading installations of volatile material. Dry break couplings for connection of loading hoses.	Emissions caused by degassing of vessels are usually not considered to be part of plant emissions.
Sampling	Emissions from sampling and from emptying of the sampling vessels.	Minor source.	Emissions from non-closed sampling points can be quantified by measuring the average loss when flushing to air and multiplying it with the sampling frequency. The sampled volume eventually released to air after completed lab analysis can be multiplied by the sampling frequency.	Closed sampling systems.	—
Combustion	Residual emissions from combustion devices resulting from incomplete combustion of fuel. Flare emissions are excluded.	Even in plants with large combustion units the unburnt fraction of the fuel from boilers and furnaces is normally a minor contributor to VOC emissions.	The amount of VOCs in the flue-gas during typical operation situations can be measured and used as an emission factor that is potentially rechecked at regular intervals. When there is no access to the stack there are general factors published, e.g. by EU.	Maintain good combustion efficiency.	This includes oxidisers used for abatement
Flares	Residual emissions of VOCs after combustion in a flare, resulting from incomplete combustion of flared gases.	Potentially a significant source for large plants;, however, accurate quantification of emissions is currently not possible.	Estimated based on an assumed combustion yield. Attempts have been made to assess actual combustion yield of flares. These depend on the flare design, the amount flared compared with the flare capacity, the wind speed, the amount of steam added to the flare, the composition of the flared gases, etc.	Best control is to minimise flaring. Good practice is to measure composition of flared gas.	Oxidising yield difficult to establish. See Section 3.5.1.6.
Sewers	Emissions from open waste water collection system, excluding emissions from waste water treatment plant equipment.	Normally a minor source. Emissions from underground gravity sewers are very low.	Often not included in emission calculations. If sewers run through open pits or lifting stations, emissions from these must be taken into account.	Minimise volatile hydrocarbons in waste water. Minimise the residence time.	—

Type of emissions source	Description	Relative contribution to total plant VOC emissions	Quantification of emissions	Control of emissions	Comments
Waste water treatment plants	Emissions from waste water treatment units (e.g. tanks, separators, dissolved air flotation).	VOC emissions from waste water treatment facilities depend on the content and volatility of VOCs in the water and on the water temperature. This contribution can be significant in some plants.	Several methods exist but the level of uncertainty of all methods is very high because of the size of the equipment and the complexity of the VOC release mechanism.	Covering waste water treatment units involves dealing with safety issues; vapour may need to be routed to abatement or used as combustion air in a boiler or furnace.	If the emissions are considered large, area measurement methods might be used. Simulation models exist but require a significant amount of sampling data. Results seem questionable in case free hydrocarbons are present.
Fugitive emissions	Emissions resulting from looseness of equipment and piping systems that are designed to be tight. The most common emission points are valve stems, flanges, pump shafts and open ends. Internal leaks of safety valves discharging to atmosphere are included in fugitive emissions and can lead to significant emissions if undetected.	Fugitives are a major source of VOC emissions for large LVOC facilities handling volatile substances. Their contribution to total VOC emissions is lower in polymer plants if finishing emissions are significant. Fugitives are generally low in OFC plants and in plants handling substances with low volatility.	Proper quantification of individual leaks requires enclosing the leak (bagging) which is not applicable in a running plant. Therefore quantification methods have been developed based on the leak detection method used. In any case, uncertainty around the quantification of fugitive emissions is very high. Quantification of internal leaks of safety valves can be done using acoustic monitoring and correlation with leak rate to calculate emissions resulting from internal leak.	Leak Detection and Repair (LDAR) programmes (see Section 3.5.4.4). Good maintenance and timely replacement of equipment. SV: Acoustic monitoring to detect internal leak through SV. Connection to flare network if feasible.	—
Accidental emissions	Emissions resulting from incidents such as spills. Safety reliefs (see above) are generally not included in accidental emissions.	Normally not significant.	Direct measurement is typically not possible due to their sudden appearance. Even if not possible to measure, records of process parameters like pressure, time and temperature are often available and can be used to give a reasonable estimate.	Avoid incidents.	—
Source: [174, CEFIC 2011]					

3.5.4.2 Techniques to prevent/reduce diffuse VOC emissions related to process and plant design

Description
Techniques to reduce diffuse VOC emissions can be considered during both phases of the design process:

- process design,
- plant design.

Process design
Process design conditions (e.g. the process temperature and pressure, and the vapour pressure of the process fluid) can influence the level of diffuse emissions. However, they are not chosen independently, they depend on other parameters (e.g. catalyst activity) as well. For example, many process streams in petrochemical plants are 'light' (containing at least 20 % of substances with a vapour pressure greater than 0.3 kPa at 20 °C) and are used at high pressure (1 500–3 000 kPa), conditions which encourage diffuse losses. On the other hand, in some operations with lower operating temperatures and pressures where the fluid vapour pressures are lower, diffuse emissions are relatively lower [121, ESA 2005].

Techniques to reduce diffuse emissions resulting from process design fall within the scopes of the other chemical BREFs (e.g. LVOC BREF and OFC BREF). Relevant techniques can be:

- to optimise the catalyst system, reactor design and physical parameters to minimise the formation of volatile side products (e.g. optimisation of the chemistry for the direct synthesis in the production of silicones to avoid the formation of light hydrocarbons);
- to achieve a balance between feed purity, processing steps, product quality and waste generation;
- to reduce the use of volatile compounds and to use products with lower vapour pressure and higher odour thresholds, e.g. in the production of OFC substances [105, COM 2006];
- to carry out solid/liquid separation (e.g. the liquid is the solvent) in such a way as to minimise VOC emissions, e.g. using centrifuges, keeping the system closed for subsequent operations (e.g. further processing or drying);
- to treat waste water streams which contain (mixtures of) VOCs by stripping, rectification and extraction or combinations of these techniques in order to remove the solvents that could contribute to diffuse emissions in further treatment operations (e.g. central waste water treatment plants) and enable their reuse.

Plant design
The selection of plant components, and the manner in which they are configured, can both greatly influence the extent of diffuse emissions. For new plants, there is a significant opportunity during the initial design phase to incorporate a wide range of techniques to reduce diffuse emissions. For existing plants, efforts can be made to incorporate many of these techniques over time as part of a process of continuous improvement.

Techniques to reduce diffuse emissions through the selection and configuration of plant components include the following:

1. Limiting the number of potential emission sources:

- to design piping layout appropriately by:
  ◦ minimising pipe run length,
  ◦ reducing the number of flanges (connectors) and valves,
  ◦ using welded fittings and pipes;
- to use, if possible, pressure transfer (e.g. gravity) to eliminate the use of pumps.

2. Maximising process-inherent containment features:

- to enclose (partially or completely) liquid effluent drainage systems and tanks used for liquid effluent storage/treatment;
- to minimise emissions during sampling by using closed sampling systems or in-line analysers;
- to install a maintenance drain-out system to eliminate open discharges from drains.

3. Selecting high-integrity equipment:

- valves with double packing seals or equally efficient equipment;
- fitting high-integrity gaskets (such as spiral wound, kammprofile or ring joints) for critical applications;
- pumps/compressors/agitators fitted with mechanical seals instead of packing;
- magnetically driven pumps/compressors/agitators.

4. Selecting appropriate materials for equipment:

- to ensure that all equipment (e.g. gaskets) is selected appropriately for each process application;
- to avoid corrosion by appropriate selection of material of construction;
- to prevent corrosion by lining or coating of equipment, painting pipes to prevent external corrosion and by using corrosion inhibitors of materials in contact with equipment.

5. Facilitating maintenance activities by ensuring access to potentially leaky equipment.

6. Collecting and treating emissions:

- conveying potentially collectable leaks (e.g. compressor seals, vents and purge lines) to flares or to flameless oxidisers.

Achieved environmental benefits
Prevention and reduction of diffuse emissions, particularly diffuse VOC emissions.

Cross-media effects
The collection and containment of diffuse emissions can lead to explosive limits being reached as a consequence of the build-up of VOCs. This issue is subject to the ATEX Directives [126, EU 2014] [131, EC 1999].

Operational data
Diffuse emissions can be estimated during process and plant design using a technique that counts the number of potential emission point sources (flanges, valves, pumps, etc.) and applies standard emissions factors relating to the contained fluid. The reliability of an emission factor in a given application depends on the quality of the factor, the specific pollutants of interest, and the type of source.

Applicability
The abovementioned techniques to reduce diffuse emissions related to process and plant design are generally applicable to all new chemical production plants. For existing plants, applicability may be limited due to operability requirements and efforts should be made to incorporate these techniques over time as part of the process of continuous improvement.

Economics
The cost of techniques to reduce diffuse emissions related to process and plant design depends on the specific installation. The costs are expected to be lower for new plants. In the long run, use of high-integrity equipment can reduce maintenance costs and time dedicated to monitoring.

Reduction of diffuse emissions often provides opportunities for raw material savings or avoiding the loss of final products, both of which result in economic benefits.

Driving force for implementation
The driving forces for implementation include:

- environmental legislation;
- reduction in material losses;
- health and safety for employees.

Example plants
All new chemical plants.

Reference literature
[81, IMPEL 2000] [105, COM 2006] [121, ESA 2005] [126, EU 2014] [131, EC 1999]

3.5.4.3 Techniques to prevent/reduce diffuse VOC emissions related to plant/equipment construction, assembly and commissioning

3.5.4.3.1 General techniques

Description
The manner in which plant components are installed can greatly affect emissions, and this is an obvious issue prior to the commissioning of a new plant. However, the reinstallation of plant components as part of maintenance or project work on plants already in operation can also have a significant impact on emissions.

Techniques to reduce diffuse VOC emissions related to plant installation can include:

- ensuring well-defined and comprehensive procedures for plant/equipment construction and assembly, including the use of the designed gasket stress for flanged joint assembly (see Section 3.5.4.3.2);
- ensuring robust plant/equipment commissioning and handover procedures in line with the design requirements (e.g. the correct gaskets have been installed, the pipe runs do not include additional flanged connections).

Achieved environmental benefits
Prevention and reduction of diffuse emissions, particularly diffuse VOC emissions.

Cross-media effects
None.

Operational data
Diffuse VOC emissions from individual plant components can be monitored as part of the plant commissioning and handover process in order to determine whether the plant has been installed correctly, and in accordance with the design.

Applicability
These techniques are applicable to all new and existing chemical production plants.

Economics
The cost of techniques related to plant/equipment installation to reduce diffuse emissions depends on the specific installation.

Reduction of diffuse emissions often provides opportunities for raw material savings or avoiding the loss of final products, both of which result in economic benefits.

Driving force for implementation
The driving forces for implementation include:

- environmental legislation;
- reduction in material losses;
- shortening the commissioning period;
- health and safety for employees.

Example plants
All new and existing chemical plants.

Reference literature
[81, IMPEL 2000] [121, ESA 2005]

3.5.4.3.2 Use of the designed gasket stress for flanged joint assembly

Description
Flanged joints consist of bolts, flanges and the gasket. In principle, all flanged joints are sources of VOCs. A differentiation between 'high leakers', which release significantly more VOCs than expected, and flanged joints, which release VOCs within an expected and accepted leak rate, can be made.

Industry standards state that flanged joints should be 'tight' enough so that no leak can be seen. Leaks (i.e. unaccepted VOCs, 'high leakers') can be corrosion on the flanges or bolts, 'sweating' gaskets, drops of the media on the flanges, etc. Independent of the type of leaks, and of the type of flanges, bolts and gaskets used in a flanged joint, the initial gasket stress during installation is the most important parameter for reducing VOC emissions. Other parameters like internal pressure and the process media do not have such a significant impact on the leak rate (see Figure 3.111). Average leak rates from process plant components demonstrate higher emission rates for light liquids compared to heavy liquids and even higher emissions for gas streams [227, CWW TWG 2009].

**Leakage test according to
EN 13555 ePTFE Gasket**

FH Münster

Gasket stress: 10.0 MPa
Leakage: 4.5×10^{-1} mg/(m·s)

p = 40 bar
T = 20 °C
He

Gasket stress: 40.0 MPa
Leakage: 5.0×10^{-4} mg/(m·s)

Source: [125, UBA DE 2009].
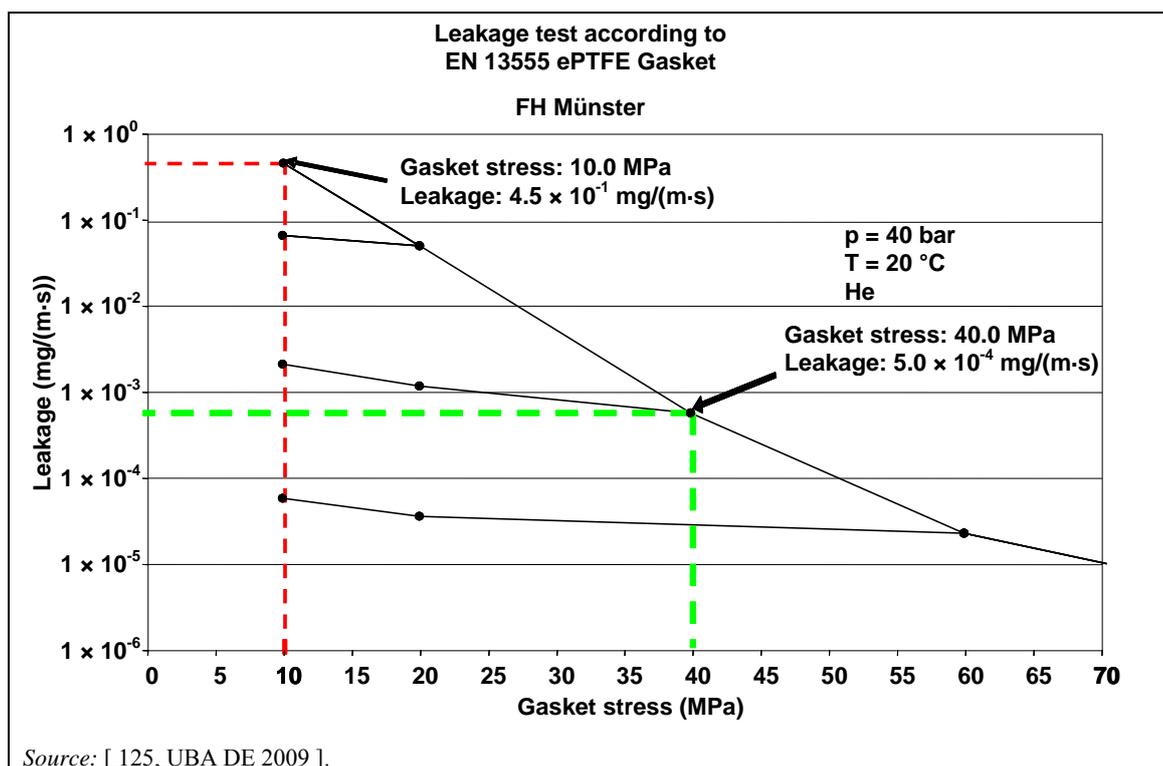
**Figure 3.111:** Leak rate and gasket stress

Figure 3.111 shows that a gasket stress of 10 MPa leads to a helium leak rate of 4.5×10^{-1} mg/(s×m). A flanged joint with a liquid medium would be considered tight with that gasket stress.

In contrast, a gasket stress of 40 MPa leads to a leak rate of 5×10^{-4} mg/(s×m). The leak rate at 40 MPa compared with 10 MPa is therefore reduced by a factor of 900 even when both gasket stresses lead to 'tight' flanged joints. This example is representative of all gasket types and PN-designated steel flanges.

To summarise, it is necessary to know the maximum allowed gasket stress to minimise VOC emissions. The pathway to reach that goal includes the following:

1)   obtaining a certified high quality gasket, e.g. according to EN 13555:2005;
2)   calculating the highest possible bolt load, e.g. according to EN 1591–1:2001;
3)   obtaining a qualified flange-assembling equipment;
4)   supervision of the bolt tightening by a qualified fitter.

The certificate for a certain gasket type indicates a high-quality gasket.

The calculation gives, on the one hand, a stress analysis for the flanged joint and, on the other hand (e.g. with EN 15911), the leak analysis. The leak analysis does not allow the calculation of the VOC emissions in real process units, but stands for the minimum bolt force to be achieved during assembly. The goal of the calculation should be (in iterative steps) to achieve the highest possible gasket stress during assembly, which depends to a great extent on the bolt-tightening method used during assembly.

A qualified flange-assembling equipment is a key element for reaching the calculated gasket stress. Controlled bolt-tightening systems with bolts above M16 are recommended. Such systems can be, for example, torque wrenches or controlled hydraulic torque systems.

The last step is a corresponding quality management system, which guarantees the high-quality assembly of the joint by qualified fitters.

The aforementioned pathway comprises an engineering approach. It has, compared to the US EPA method, the significant advantage of avoiding VOC emissions right from the start and in the end saves money due to reduced lost process media, increased safety against blowout of the gasket (due to higher gasket stress in service) and reduced downtime of process units due to improved availability.

Achieved environmental benefits
The environmental benefits will be achieved by significantly reduced VOCs being emitted from flanged joints. As shown in Figure 3.111 which is representative of standard PN-designated steel flanges (class-designated flanges reach even higher gasket stresses but not necessarily lower leak rates as the effective gasket width will be higher due to lower flange rotation), the leak rate can easily be significantly reduced (by several orders of magnitude). Essential steps for reaching these goals are listed as 1) to 4) above.

Taking the example of Figure 3.111, a DN50-PN40 (two-inch) flange installed with 10 MPa initial stress has VOC emissions of 3.12 kg/yr (helium); installed with 40 MPa, the emissions are 0.0035 kg/yr. There are far more flanges and larger diameters in the chemical and petrochemical process units than shown in the example given.

The calculation above is only an example and does not mean that 40 MPa has to be reached or 10 MPa is a certain minimum. It only shows that 'tight' (10 MPa gasket stress) can easily become improved upon when a higher gasket stress is reached during assembly.

Besides the environmental benefits, the described procedure includes a greater safety margin and longer timespans between downtime periods.

Cross-media effects
No cross-media effects are expected.

Operational data
Laboratory tests and many research reports/projects from universities and companies prove that sufficient high gasket stresses and the pathway mentioned above lead to the described effects of lower VOC emissions, improved safety and reduced downtime periods.

Applicability
The technique can be applied to all process units in the petrochemical and chemical industry, and the pulp and paper industry as well as in power plants.

Economics
The investment costs are normally marginal as the 'TA Luft' certificate (only mandatory in Germany) comes from the gasket manufacturer. Calculations should be performed anyway (often without state-of-the-art calculation codes). Assembly with a standard spanner is not less expensive than assembly with torque wrenches. On the other hand, there can be savings expected from reduced losses of process media, improved safety of flange joints and therefore reduced downtime periods.

Driving force for implementation
New European standards and national standards will become more and more important. The up-to-date calculation standard EN 1591–1:2001 and any other calculation code which allows the calculation of the highest possible bolt load (which has to be reached during assembly) will lead to lower VOC emissions. However, the calculation alone does not result in reaching the overall goal. It is, in fact, mandatory to combine the items 1) to 4) mentioned above.

Example plants
No information provided.

Reference literature
[125, UBA DE 2009] [227, CWW TWG 2009]

3.5.4.4   Leak detection and repair / monitoring of diffuse VOC emissions with sniffing and OGI

Description
Fugitive VOC emissions can be reduced by the detection and subsequent repair or replacement of leaking components. This is achieved by adopting a structured approach, commonly known as a leak detection and repair (LDAR) programme. An LDAR programme is usually risk-based and includes two fundamental steps:

- identification of the leaking components,
- repair of these leaks in order to minimise losses.

Leak detection
Two methods are currently available for the identification of leaks, and each method has its individual strengths and weaknesses. It is therefore necessary to decide upon the purpose behind a measurement exercise when selecting the method. In some circumstances, methods might need to be combined to fully understand the leak levels. Large-scale methods (see Section 3.5.4.5.) may quickly locate the major emission areas but not be able to identify individual fugitive emission sources. Maintenance may be improved using infrared cameras to locate the leakers.

1. Method EN 15446: Sniffing

Leak detection using hand-held analysers is called 'sniffing'. This method identifies leaking components by measuring the concentration of hydrocarbon vapours (in ppm) in the immediate vicinity of the leak with a flame ionisation detector (FID), a semi-conductive detector or a photoionisation detector (PID). The selection of the most suitable type of detector depends on the nature of the substance to be detected.

To check each potentially leaky component with hand-held analysers is time- and cost-intensive. Moreover, some leaking points in a plant might be difficult or impossible to access with the hand-held detectors to obtain a measurement. Sniffing surveys need careful preparation and are usually executed in campaigns that cover a specified portion of the plant. Some companies have therefore developed a **'targeted monitoring'** approach in which additional emphasis is put on components with a higher tendency to leak.

2. Optical gas imaging (OGI) method

The optical gas imaging method involves the detection of leaks with advanced hand-held infrared cameras that are specially developed for this purpose. Both active and passive systems exist: active systems use an adequately tuned laser beam, while passive systems detect infrared radiation reflected by the equipment. Gas imaging based on passive cameras was introduced in the early 2000s, and enables direct visualisation of both the leak and the leaking component and the recording of the images. In these recordings, gas clouds are visible as light or dark plumes.

Direct visualisation of leaks is of great value to improve the efficiency of equipment maintenance as only the leaky equipment is repaired. Another advantage of the camera is the possibility to detect leaks under insulation and to screen from a distance, so that VOC emissions from components not accessible for sniffing can be located and repaired. OGI is mainly used at larger installations/units.

Infrared cameras are tuned to detect specific molecular bonds. Therefore, the limit of detection depends on the type of molecule. In 2012, the sensitivity of infrared cameras was lower than that of traditional sniffing equipment. They work particularly well with alkanes, but less so with BTEX.

Some plants are using infrared cameras before start-up to ensure the process is tight (i.e. by pressurising the equipment). Others are using cameras for safety purposes and for searching for large leaks.

Optical gas imaging techniques are gaining in popularity. Their ability to detect the most significant fugitive VOC emissions has been confirmed in field trials and the US EPA considers that over a number of years an equivalent reduction of fugitive VOC emissions can be achieved compared to the use of sniffing methods [127, US EPA 2008].

However, at the beginning of 2014, no standards were available that ensure the comparability of OGI measurements between different instruments and/or users. However, such standardisation has started at CEN following a mandate given by the European Commission in 2012 [168, COM 2012].

Leak repair

A staged approach is often applied to the repair of leaks:

- An initial intervention such as tightening bolts to eliminate leaks from valve stems or flanges, installing tight caps on open ends. Such an intervention needs to be performed by skilled operators taking the necessary safety precautions.
- Equipment with leaks that cannot be stopped by minor interventions needs to be repaired. This may involve changing gaskets or packing, and may therefore require the equipment to be taken out of service.
- When no effective repair can be performed, replacement of the equipment should be considered.

The LDAR programmes based on sniffing typically do not include tanks and plant areas that are difficult to access. OGI and whole plant measurements (see Section 3.5.4.5.) will identify problem areas that are not being monitored and allow them to be addressed. In many instances, they allow for more efficient allocation of maintenance efforts by targeting the areas of highest emissions first.

Achieved environmental benefits
Prevention and reduction of fugitive VOC emissions.

Cross-media effects
None.

Operational data
No information provided.

Applicability
LDAR is applicable to plants that handle VOCs. LDAR is usually implemented in a risk-based way, i.e. plants with high-integrity equipment require less stringent LDAR application.

Economics
The investment costs for an analyser were reported to be EUR 5 000–20 000 for sniffing and EUR 70 000–100 000 for OGI. During operation, the main difference is the time required for surveying. When using sniffing methods, only about 500 components can be checked per day by a surveying team. In contrast, optical gas imaging techniques allow 15 000 to 20 000 components per day to be surveyed. Therefore, sniffing methods are generally less expensive in the case of small installations, while OGI is less expensive in the case of large installations [140, CEFIC 2008].

In a typical US refinery or large petrochemical plant with over 200 000 regulated components, the annual cost for an LDAR programme is reported to exceed EUR 750 000 (actual cost USD 1 000 000, average currency conversion rate for 2010: EUR/USD = 1.329) with the US EPA Method 21 based on sniffing.

Driving force for implementation
The driving forces for implementation include:

- environmental legislation;
- reduction in material losses;
- health and safety for employees.

Example plants
LDAR programmes are widely used at petrochemical installations and refineries.

Reference literature
[81, IMPEL 2000] [121, ESA 2005] [127, US EPA 2008] [140, CEFIC 2008] [168, COM 2012] [209, Energy Institute 2010] [211, US EPA 2006] [215, INERIS 2010]

3.5.4.5 Monitoring of diffuse VOC emissions with DIAL and SOF

Description
In order to assess the effectiveness of all the techniques applied to prevent/reduce diffuse VOC emissions, two monitoring methods are available for use as described below.

1. Differential absorption LIDAR (DIAL) method
The DIAL method can target one or two species at a time. It can be used to estimate VOC concentrations in general by targeting a generic wavelength that is representative of the carbon-hydrogen bond within the species of interest. This generic measurement will yield information on C_2 to C_8 compounds.

DIAL systems have both an infrared and an ultraviolet component. The infrared DIAL is used primarily for alkanes although it can identify most species with absorption in the infrared spectral region between 2.5 µm and 4 µm – including, for example, hydrogen chloride, nitrous oxide, and methanol. Limits of detection for the alkanes are in the 10–50 ppb range at distances up to about 800 metres. The UV/Visible DIAL can identify and specify benzene, toluene, and xylenes in the 10–20 ppb range and can also be used for measuring elemental mercury, ozone, sulphur dioxide, nitrogen dioxide, and nitrogen monoxide.

Limits of detection are very dependent upon site conditions at the time of measurement. During a verification project done by the UK National Physical Laboratory, it was reported that the DIAL measurements for a known methane release were within ±10 % of the true values. In other experiments, the DIAL measurements were within ±12 % of the true value of an aliphatic hydrocarbon plume and within ±15 % of a toluene plume [211, US EPA 2006]. To obtain mass emission fluxes, the concentration data across the plume section are multiplied by the wind velocity perpendicular to the measurement plane. Wind data availability, accuracy and representativeness are essential for reducing measurement uncertainties. The overall uncertainty in industrial field conditions is evaluated at around 30–50 %, most of it originating from wind speed evaluation [116, COM 2015].

The DIAL method may provide a conservative estimate because it does not necessarily capture the whole plume. Nonetheless, DIAL studies of 100-plus facilities executed under different climatic, environmental, and operating conditions all show that the facility has higher emissions than are reported [211, US EPA 2006].

2. Solar occultation flux (SOF) method
The solar occultation flux (SOF) method uses a passive FTIR system mounted in a truck. This method measures olefins and alkanes, but not aromatics. Also, some other restrictions exist on the range of hydrocarbons that can be measured, i.e. those heavier than C_8 to C_{10}. Its use is limited to sunny days, and the wind must blow in the same direction for a long period of time.

The overall uncertainty for quantification in industrial field conditions is evaluated at around 35–40 %. Most of it originates from wind (speed and direction) evaluation uncertainty and retrieval uncertainty (combined effect of instrumentation and retrieval stability on the retrieved total columns during the course of a plume transect).

While each approach is different, the DIAL and SOF methods both produce roughly equivalent emission estimates.

Achieved environmental benefits
The facilitation of the prevention and reduction of diffuse VOC emissions.

Cross-media effects
None.

Operational data
In Sweden, both DIAL (until 1988, once every three years) and SOF (after 1998) methods have been used to make site level assessments at petrochemical installations.

Applicability
Applicable to all petrochemical sites.

DIAL and SOF can be used for the overall quantification of diffuse VOC emissions, but they show limitations in the accuracy of the localisation of specific emission sources [81, IMPEL 2000] [174, CEFIC 2011].
The commercial availability of DIAL and SOF is limited in some EU Member States.

Economics
Depending upon the size of the site, a typical DIAL survey cost is reported to be between EUR 75 000 and EUR 150 000 (actual cost between USD 100 000 and USD 200 000, average currency conversion rate for 2010: EUR/USD = 1.329).

Driving force for implementation
The driving forces for implementation include:

- environmental legislation;
- reduction in material losses;
- health and safety for employees.

Example plants
Petrochemical installations and refineries in Sweden.

Reference literature
[81, IMPEL 2000] [116, COM 2015] [121, ESA 2005] [174, CEFIC 2011] [209, Energy Institute 2010] [211, US EPA 2006] [215, INERIS 2010]

3.5.5 Odour emissions

3.5.5.1 Overview

[195, ADEME 2009] [196, ADEME 2005] [197, DEFRA 2010]

Odour (see definition in the Glossary) pollution is related to the emission of a large number of chemical compounds, mainly:

- **sulphur** compounds (e.g. hydrogen sulphide, mercaptans, sulphides, disulphides);
- **nitrogen** compounds (e.g. ammonia, amines, heterocyclic compounds);
- **oxygen** compounds (e.g. organic acids such as acetic acid, aldehydes such as formaldehydes, ketones and alcohols);
- **hydrocarbons**.

Many industrial and non-industrial sectors are sources of odour emissions such as the intensive farming sector, the food processing sector, slaughterhouses, waste water treatment, waste treatments, pulp and paper production, refineries, and the chemical and petrochemical industries. Also, the storage and handling of waste, sludge (see in particular Section 3.4.2 on sludge treatment techniques), slurry and chemicals are often a source of odour pollution. In addition, occasional operating failures at facilities pertaining to these sectors can lead to short-term odour problems.

The subject of odour is complex due to the fact that:

- odour can arise from a single substance or from a combination of substances;
- in combination with other substances, the characteristic odour of a single substance can be modified so as to be unrecognisable;
- odour from a combination of substances changes as the mixture becomes diluted and the concentration of each substance falls below its odour threshold;
- odours from a substance or mixture of substances can be pleasant when dilute or offensive when concentrated;
- odours that are pleasant or acceptable to one nose can be offensive to another;
- people have different odour thresholds, so odours that are detected by one person may not be detectable for another.

Also, compared to other types of pollution, odour pollution presents certain peculiarities.

- The very low limits of detection of some odorous compounds require measurement systems with high performance levels (odour can be detected by the human nose when the concentrations of known odour-causing substances are close to zero, e.g. 0.0005–0.001 mg/m^3 for mercaptans, 0.025 mg/m^3 for H_2S, 1 mg/m^3 for formaldehyde). Odour threshold values for over 150 VOC substances can be found in the LVOC BREF [104, COM 2003].
- Specific emission limit values exist for odour pollution in some Member States.

The choice of techniques to use for measuring and treating odorous pollution may be difficult. This is because, contrary to other types of pollution which can be measured and treated in a relatively simple way, measuring odours is complex due to the subjectivity and aleatory characteristics of odour. This has an effect on the choice and sizing of an installation designed to treat odour pollution. However, there are techniques proven to deal with odour problems and these are mentioned in Section 3.5.5.4.2.

3.5.5.2 Odour management plan

Description
An odour management plan (OMP) is part of the environmental management system (EMS) of the installation (see Section 3.1.2) and includes all of the following elements:

- a protocol containing appropriate actions and timelines;
- a protocol for conducting odour monitoring;
- a protocol for response to identified odour incidents;
- an odour prevention and reduction programme designed to identify the source(s), to measure/estimate odour exposure, to characterise the contributions of the sources and to implement prevention and/or reduction measures.

The approved OMP may be made available to the public.

Achieved environmental benefits
The minimisation of odorous emissions is the achieved environmental benefit.

Cross-media effects
There are no cross-media effects associated with the implementation of this technique.

Operational data
No information provided.

Applicability
The technique is applicable to new and existing installations provided that an odour nuisance can be expected or has been substantiated.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
No information provided.

Reference literature
[197, DEFRA 2010] [201, Environment Agency (England and Wales) 2010] [204, Environment Agency (England and Wales) 2011]

3.5.5.3 Odour monitoring

3.5.5.3.1 Overview
[101, COM 2016] [195, ADEME 2009] [196, ADEME 2005]

Odour monitoring is carried out using analytical methods (i.e. physical and chemical analysis) or sensorial approaches. Sensorial analyses, being assigned to the 'human sensor', are the cause of significant uncertainties.

The techniques can be classified into three categories:

- for odour concentration determination (expressed in ou_E/m^3, to control limit values): dynamic olfactometry (see Section 3.5.5.3.2);
- for odour perception in the surrounding area (impact): odour surveys (see Section 3.5.5.3.3), odour intensity mapping (see Section 3.5.5.3.4), and odour wheels (see Section 3.5.5.3.5);
- for self-monitoring: electronic noses (see Section 3.5.5.3.6).

To determine the odour concentration, an air sample must be taken. The sampling techniques are similar to those used for measuring individual compounds.

Odour monitoring is carried out where odour nuisance can be expected or has been substantiated.

3.5.5.3.2 Dynamic olfactometry

Description
Odour concentration is determined by a panel of trained human assessors or panellists. Odour concentration is measured according to the European standard EN 13725:2003 [219, CEN 2003]. It is independent of humans' knowledge of odorous substances since the human nose reacts to every odorous gas above the limit of detection.

The basis of this measurement method is that odour can be detected by a person if the individual odour threshold is exceeded.

The gaseous sample of odorants is directly collected on site using the 'lung principle' to prevent the sample from being polluted by the pumping system used to collect it. The gas is collected in specific odour-free bags avoiding adsorption on its inner surface. The odour concentration is

determined by dynamic olfactometry, i.e. by presenting a panel of selected and screened human subjects with that sample, varying the concentration by diluting the sample with odour-free gas in order to determine the dilution factor at the 50 % detection threshold (that is when the odour can just be perceived by 50 % of the test panel). The numerical value of the odour concentration is equal to the dilution factor that is necessary to reach the odour threshold for that sample. Its unit is the European Odour Unit per cubic metre (ou_E/m^3) under standard conditions for olfactometry (101.3 kPa, 293 K). Therefore, the odour concentration at the odour threshold is $1\ ou_E/m^3$ by definition.

The members of the panel must fulfil certain requirements, for example regarding their sensitivity to *n*-butanol.

To ensure the required level of accuracy, odour concentration is determined by a panel composed of six to eight members. The laboratory must be ventilated to isolate the panellists from the ambient environment odour. Samples must be analysed within 24 hours of sampling.

Physico-chemical and olfactometric analyses are complementary in order to determine operation parameters responsible for the emissions.

Achieved environmental benefits
The achieved environmental benefit is the facilitation of the minimisation of odorous emissions.

Cross-media effects
There are no cross-media effects associated with the technique.

Operational data
The inaccuracy of this method for dilution factors below 30 limits its use for environmental odour concentration determination (i.e. off site). When the odour flow rates of the main emitters of the installation are known, odour dispersion modelling is often preferred to estimate the odour impact of the plant.

This method can be used to determine the higher emitters on installations that correspond to diffuse or ducted emissions by determining the odour flow rates. These data are obtained, for example:

- by multiplying the odour concentration with the gas flow rate for a ducted source;
- by multiplying the odour concentration with the renewing air rate per hour for a volumetric source;
- directly by handling the samples through the air flux chamber.

Applicability
The technique is applicable to new and existing installations.

Advantages and disadvantages are given in Table 3.302.

Table 3.302: Advantages and disadvantages associated with dynamic olfactometry with human assessors

Advantages	Disadvantages
- Samples are quite easy to take - Results are given by human subjects in relation to the perception of the population - Limit values can be imposed for major sources in order to minimise emissions - A complementary method for the chemical analysis	- Discontinuous measurement - As the pollutants present in the sample are unknown, some safety precautions must be taken to avoid any negative effect on panellists' health - The uncertainty of the method is not known (test on real gaseous samples are performed)

Economics
The cost of one analysis is in the range EUR 300–400.

Driving force for implementation
The technique is used at installations/units that must respect odour emission limits when odour nuisance is an issue or when complaints occur in the vicinity of the installation/site.

Example plants
The technique is reported to be used in sectors such as waste water treatment plants, animal by-products facilities, and composting plants.

Reference literature
[207, INERIS 2009] [219, CEN 2003]

3.5.5.3.3   Odour surveys

Description
Odour annoyance is a subjective concept. Its assessment should be based on residents' reports and behaviour. Annoyance results from a number of factors including concentration/intensity of odours, duration of exposure, frequency of occurrence, offensiveness (hedonic tone), expectation of the receptors and psycho-sociological factors influencing personal perception of and behaviour towards an odour.

Odour annoyance is assessed by the use of different questionnaire techniques. Questionnaires are filled in regularly by volunteer residents to evaluate the perceived nuisance. The answers are correlated with meteorological conditions to link the plant's emissions to the nuisance described.

The respondents rate the odour perception, the quality, and the feeling of annoyance on a five-point scale:

- 'definitely not annoying',
- 'slightly annoying',
- 'annoying',
- 'very annoying',
- 'extremely annoying'.

Conducting a survey requires enough responses to carry out a statistical analysis. Therefore, this investigation can last quite some time (six months to one year) and requires numerous observations and enough residents spatially sampled considering the distances of impacts (less concentrated inversely to the distance to the plant).

Representative sampling observations (in space and time) are obtained by considering, in particular, the population density, the direction and the velocity of the prevailing winds, and the theoretical impact distances (determined by odour dispersion modelling).

An odour nuisance survey within the community surrounding the installation/site is undertaken prior to the commencement of commissioning activities in relation to the installation/site, and at regular intervals (e.g. yearly) thereafter.

The surveying instrument (questionnaire) is developed and approved prior to its use.

Results are collated and summarised in regular environmental statements (see Section 3.1.2), and are utilised as part of the odour management plan (see Section 3.5.5.2).

Achieved environmental benefits
The facilitation of the minimisation of odorous emissions is the achieved environmental benefit.

Cross-media effects
There are no cross-media effects associated with this technique.

Operational data
Odour surveys by a committee of residents can allow better knowledge of the conditions under which odour annoyances can occur. Such knowledge can lead to changes in plant configuration and operations to reduce odour nuisances.

The parameters which have to be assessed to limit odour impacts can be determined and recommendations can be proposed, e.g. specific on-site practices to be avoided under characteristic meteorological conditions, defining adapted prevention or abatement techniques considering the main sources which contribute to annoyance.

Conducting an odour survey by a committee of residents can lead:

- to determining the variables that have an impact on odour annoyance (emissions, meteorological conditions, specific operations);
- to determining and comparing annoyance-free periods to periods of annoyance;
- to designing an assessment and survey tool to determine the degree of annoyance in the neighbourhood of a plant;
- to keeping a record of the malodorous events in order to gain a good understanding of the main factors leading to annoyance and complaints.

The requirements for conducting an odour survey by a committee of residents are listed below.

- Having enough volunteers to perform a relevant statistical analysis.
- Being able to motivate respondents during a period lasting from a few months to one year.
- A careful analysis of data, e.g. taking into account inaccuracies in the reporting of odour incidents. The responses to the questionnaires must be treated according to the meteorological conditions (speed and wind direction) to control that the respondent is downwind of the installation when they give positive responses.
- A questionnaire (the surveying instrument) must be developed according to the aim and the duration of the study. For example, to evaluate an annual perception percentage, some specific data could be useful such as the correlation between no declared perception because of absence or no perception during that period.

Complementary methods can be used to qualify and describe the perceived odour in order to determine what the odour sources are that are responsible for the annoyance. Implementing this technique involves putting a training programme in place for the volunteers and regularly debriefing them.

The training programme should allow participants to identify the odours likely to occur in the neighbourhood of a plant and especially the ones from the surveyed site. It should also allow participants to qualify the different odours they perceive in their life even if not related to the observed facility.

This technique can also play a role in controlling the efficiency of odour abatement techniques.

The surveying instrument (questionnaire) is developed and approved prior to its use. In France, this method is often associated with a local odour management group made up of representatives of plant operators, the local community (including volunteer residents) and local public authorities. A specific meeting to approve of the questionnaire can be organised with other public authorities.

Applicability
The techniques are applicable to new and existing installations. It can also be useful in a baseline monitoring programme.

Economics

The costs of conducting an odour survey with a committee of residents are in the range EUR 20 000–30 000 for a 6-month study including recruitment of volunteers, management of questionnaires (by post, internet or phone), analysis of the filled-in questionnaires, and meeting management for the presentation of the results to the residents and other interested parties near the plant. All of this can be managed by an external consulting firm.

Equipment needed generally includes a PC, statistical software, and a weather station at a cost of about EUR 10 000.

Driving force for implementation

The driving forces for implementation include:

- legislation;
- complaints occurring in the vicinity of the installation/site.

Example plants

The technique is reported to be used at chemical plants where complaints occur. The technique is widely used in the Netherlands [228, CWW TWG 2011].

Reference literature

[208, INERIS 2009] [228, CWW TWG 2011]

3.5.5.3.4 Odour intensity mapping

Description

In some circumstances, odours can be a source of annoyance that will necessitate the measurement of their intensity. The direct measurement of the smell intensity perceived from a gaseous sample is determined according to the French standard NF X43–103. This method of olfactory equivalencies (or comparative method) consists of comparing the odour intensity of a determined sample with a reference scale based on different intensities. This reference scale establishes an orderly series of concentrations of a pure body, for example, of 1-butanol. The NF X43–103 standard is used for different applications such as materials selection and environmental studies. The measurement methodology is based on the comparison of the odour perception with a standard substance scale in order to determine the intensity of the odour. The panel is constituted of six to eight members. For field measurements, measurement points are defined according to the impact distances of the plant and the direction and velocity of the prevailing winds. Meteorological conditions are registered during measurements. Intensity perception can then be correlated with the examined plant. Special care must be taken for panellists' health.

Achieved environmental benefits

The achieved environmental benefits of using odour intensity mapping are:

- establishment of an olfactory reference state of the environment before installing a plant;
- establishment of the olfactory impact of a plant by comparison with the reference state;
- control of the efficiency of the employed treatment techniques on perception;
- control of the reduction of impact;
- assessment of the intensities perceived in the environment of an industrial sector.

Cross-media effects

There have been no cross-media effects reported with the use of this technique.

Operational data

The results map presents the olfactory impact, expressed in intensity, of a plant on the surrounding environment. The intensity is determined on a scale from 1 to 4, from low to very high according to the intensity perceived with the reference scale determined by selected *n*-butanol concentrations in water.

The odours are described as having the characteristics of a rural environment, an urban environment or an industrial environment.


Source: [220, INERIS 2009]
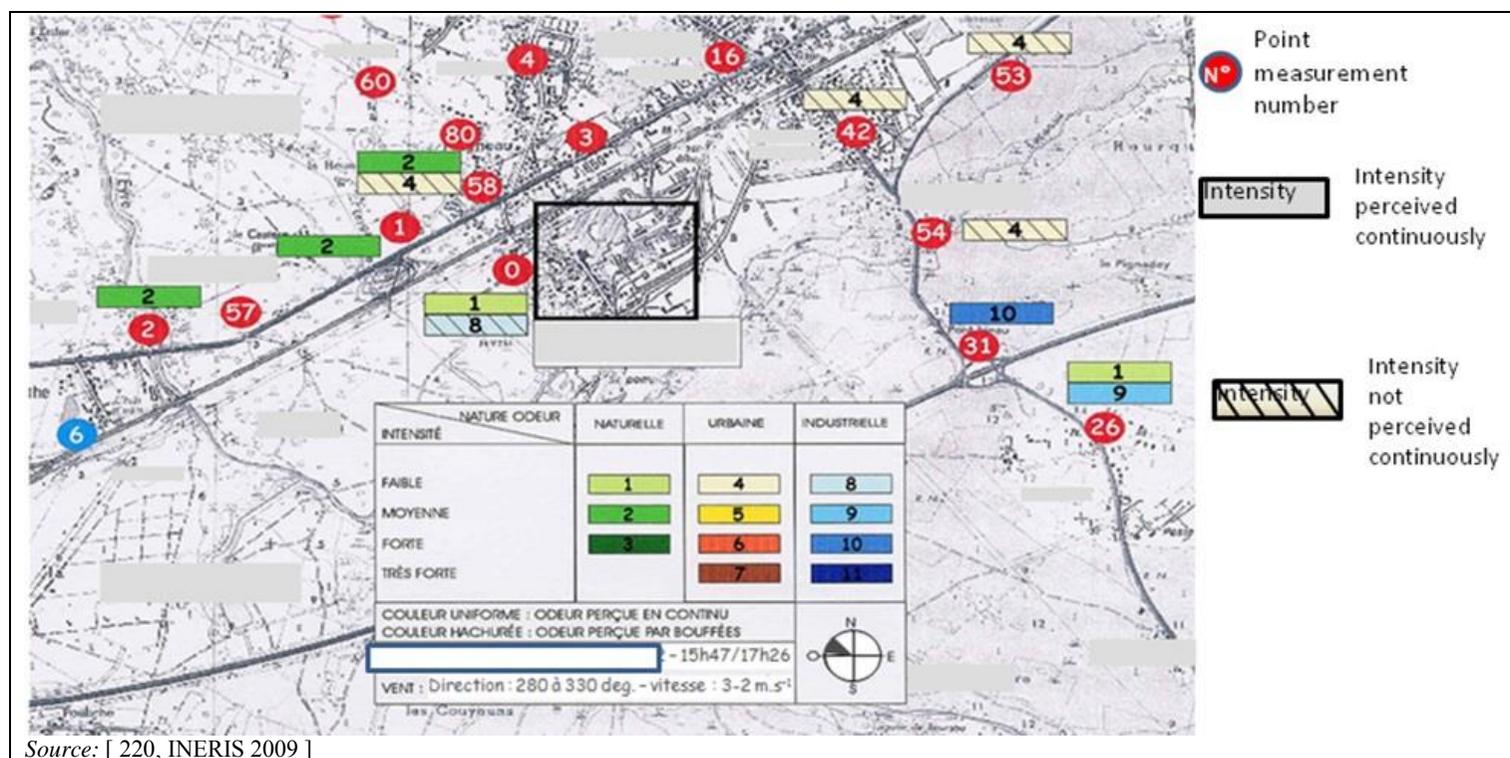
Figure 3.112: **Olfactory impact (in terms of intensity) of an industrial plant on the surrounding environment**

This method is complementary to the community survey for the assessment of annoyance. Here, the panellists are trained to classify the perceived intensities and their reactions are independent of the olfactory state of the environment.

Applicability
Applicable to future plants to establish an olfactory reference state of the neighbourhood. Applicable to new and existing plant of all sizes.

Economics
Odour intensity determination of a gaseous sample in the laboratory costs around EUR 300. Field measurements (two campaigns for two wind conditions and the panellists' selection) cost around EUR 10 000.

Driving force for implementation
To evaluate the potential impact of the plant evolution, or when complaints occur in the neighbourhood.

Example plants
Method mainly used in France, Belgium and Switzerland. In France, field measurements are realised on odorous facilities in several sectors but not usually in chemical plants (establishing an olfactory reference before installing the plant is recommended by the French regulation).

Reference literature
[220, INERIS 2009]

3.5.5.3.5 Odour wheels

Description
Odour wheels are used to evaluate and classify the character and intensity of odours. They attempt to link commonly used descriptors of odours around industrial (e.g. chemical) installations or sites with the most likely chemical cause/or origins.

The use of odour wheels can facilitate discussions about odour problems between operators, public authorities and the public.

Odour wheels are based on flavour profile analysis (FPA) sensory panel testing to define odour characteristics and related odour intensities. The intensity or strength of each odour characteristic is reported on a seven-point scale.

Achieved environmental benefits
The facilitation of the minimisation of odorous emissions is the environmental benefit associated with the development and use of odour wheels.

Cross-media effects
There are no cross-media effects associated with the technique.

Operational data
No information provided.

Applicability
The technique is applicable to new and existing installations.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
No information provided.

Reference literature
[197, DEFRA 2010] [212, Suffet and Rosenfeld 2007]

3.5.5.3.6   Electronic noses

Description
Electronic noses are apparatuses that mimic the human sense of smell. Typically, they include an array of sensors used to detect and distinguish odours in complex (air) samples. Electronic noses include three major parts: a sample handling system, a detection system and, a data processing system.

The **sample handling system** enables the generation of the headspace (volatile compounds) of a sample, which is the fraction analysed for odours. The system then injects this headspace into the detection system of the electronic nose. The sample handling system is essential to guarantee the quality of the analysis.

The **detection system**, which consists of an array of sensors, is the 'reactive' part of the instrument. When in contact with volatile compounds, the sensors react, which means they experience a change of electrical properties. Each sensor is sensitive to all volatile molecules but each in their specific way. Most electronic noses use sensor-arrays that react to volatile compounds on contact: the adsorption of volatile compounds on the sensor surface causes a physical change in the sensor. A specific response is recorded by the electronic interface transforming the signal into a digital value. Recorded data are then computed based on statistical models. The more commonly used sensors include the metal oxide semiconductor (MOS), conducting polymer (CP), quartz crystal microbalance (QCM), surface acoustic wave (SAW), and the metal oxide semiconductor field-effect transistor (MOSFET). In France, an electronic nose is commonly equipped with six sensors. In recent years, other types of electronic noses have been developed that utilise mass spectrometry or ultra-fast gas chromatography as a detection system.

The **data processing system** works to combine the responses of all of the sensors, which represent the input for the data treatment. This part of the instrument performs global fingerprint analysis and provides results and representations that can be easily interpreted. Moreover, the electronic nose results can be correlated to those obtained from other techniques (e.g. sensory panel, gas chromatography, mass spectrometry).

As a first step, an electronic nose needs to be 'trained' with qualified samples so as to build a database of references for odours. The instrument can then recognise new samples by comparing volatile compound fingerprints to those contained in its database. Thus they can perform qualitative or quantitative analysis.

The 'training process' or 'learning process' consists of the following steps.

- Samples are taken on site and analysed by olfactometry. The samples are then presented to the electronic nose in order to develop a mathematical model that is able to convert the raw sensor data into odour concentration. It is necessary to perform a reasonable number of parallel measurements with the electronic nose and via olfactometry (i.e. measurement of odour according to standard EN 13725:2003).
- Determination of the correlation between the characteristic electronic nose responses and the expected odour concentration values established by olfactometry for the samples taken on site. According to the odorous compounds that constitute the emissions to survey, this correlation could be very difficult to establish or could be established with a great uncertainty.

Electronic noses are equipped with wireless communication systems in order to transmit data in real time to an office computer. This allows operators to take rapid actions should an odour incident occur.

Even if already used in industry, electronic noses is a technique still under development.

Achieved environmental benefits
The facilitation of the minimisation of odorous emissions is the achieved environmental benefit.

Cross-media effects
There are no cross-media effects associated with the technique.

Operational data
Ambient air is sampled continuously in the sensor chamber of an electronic nose. The sensor signal can be sampled every second.

An electronic nose is 'trained' to survey characteristic emissions in quality and for a range of odour concentrations. That is to say that an electronic nose 'trained' for certain sources of odours cannot be used to monitor other sources or another plant without a new adapted 'learning programme'.

Electronic noses can be trained to give results in odour intensity or in chemical concentration for example. A referential method must exist to establish a correlation ratio.

This method must be improved for different types of emissions (odorous compounds involved) and their potential modification over time according to the expected decrease of the gaseous emissions.

Applicability
Electronic noses are applicable to new and existing installations after the careful 'training' programme of the equipment.

Advantages and disadvantages are given in Table 3.303.

Table 3.303: Advantages and disadvantages associated with electronic noses

Advantages	Disadvantages
• Real-time monitoring of odours is possible, enabling quick reactions from plant operators • High sensitivity and correlation with data from human sensory panels for several applications • Once correctly installed and calibrated, relatively cheap to operate	• Relatively complex system to put in place and to maintain adequately calibrated • Many current electronic nose instruments suffer from problems with reproducibility with varying ambient temperature and humidity

Economics
Investment costs for the electronic nose, a weather station and the necessary software are estimated to be EUR 25 000–30 000.

Costs relating to the 'learning programme' (based on the collection and analysis of 15 samples for the construction of the mathematical correlation model to express electronic nose results in odour concentrations) and to the control of the system (based on 5 samples) are estimated to be EUR 30 000.

Driving force for implementation
Electronic noses are installed when complaints occur in the vicinity of the installation/site or when a local odour management group (e.g. made up of representatives from the operator, local community and local public authorities) recommends it.

French regulations allow plant operators to decrease the frequency of olfactometric measurements when electronic noses are used.

Example plants
The technique is reported to be used in the sectors such as composting plants, animal by-products facilities and the food industry.

Reference literature
[205, INERIS 2009] [206, Peris and Escuder-Gilabert 2009]

3.5.5.4 Techniques to prevent/reduce odour emissions from waste water collection and treatment and from sludge treatment

3.5.5.4.1 General techniques

Description
The anaerobic decomposition of organic matter in waste water treatment plants (WWTPs) or during sludge treatment results in the generation of odours. These originate from the collection, storage and treatment systems. The decomposition of sulphur compounds in particular can give rise to odorous emissions of hydrogen sulphide (H_2S) and mercaptans, while the breakdown of nitrogen compounds can in particular give rise to odorous emissions of ammonia and amines. These odours are emitted through the volatilisation of organic compounds at the liquid surface.

In WWTPs, odour emissions can be influenced by different factors, such as waste water composition, treatment methods and treatment conditions (e.g. temperature, pH, retention time). In general, different compounds dominate the odour emissions from different treatment processes. For example, H_2S is generally associated with inlet works emissions, while mercaptans are associated with sludge treatment processes.

In general, the first steps of the waste water treatment process (prior to biological treatment) are the ones with the highest odour emissions and the major odour source of a WWTP is represented by the primary sedimentation. This highlights the importance of the sewer system, which influences the quality of the waste water at the plant inlet and therefore its odour emission capacity. For this reason, the operating conditions of the waste water treatment plant itself generally have less influence on odour emissions from the first treatment steps than the correct management of the sewer system [202, Capelli et al. 2009].

The techniques given below can be used to minimise odour emissions at a waste water treatment plant:.

- minimise the residence time of waste water and sludge in collection and storage systems, in particular under anaerobic conditions;
- use of chemicals to destroy or to reduce the formation of odorous compounds (e.g. oxidation or precipitation of hydrogen sulphide);
- optimise the aerobic treatment, e.g. by controlling the oxygen content, frequent maintenance of the aeration system, use of pure oxygen and/or removal of scum in tanks;
- cover or enclose facilities for collecting and treating waste water and sludge to collect the odorous waste gas for further treatment;
- end-of-pipe treatment (see Section 3.5.5.4.2).

Achieved environmental benefits
The reduction of odorous emissions from WWTPs is the achieved environmental benefit.

Cross-media effects
The cross-media effects associated with the abatement techniques used (e.g. scrubber, incinerator/oxidiser) are described in the section of the BREF relevant to each specific technique. Management-type techniques have no cross-media effects. Removing surface scum and skimmings in waste water treatment tanks entails the use of energy.

Operational data
Operational data from several German WWTPs are given below.

Plant A
Because anaerobic conditions cannot be ruled out, waste gases from trickling filters are exhausted and incinerated (under autothermic conditions, with 5 % methane content). After reconstruction of the WWTP, the primary treatment tanks, the neutralisation tank, the central pumping station and the anaerobic reactor have been enclosed. Waste gases from this equipment are treated by alkaline scrubbing (with NaOH) and activated carbon.

Plant B
High tower biology and trickling filters are enclosed. Waste gases from this equipment are treated by scrubbing. An additional measure for minimising odours and other gaseous emissions includes the addition of lime to the sludge arising from the final clarification stage (thus increasing its pH to 11).

Plant C
Part of the waste gas from the WWTP (i.e. from the sludge thickener) is fed to the sludge incinerator as combustion air (a scrubber is on standby should the incinerator not be used). Additional measures for minimising odorous and other gaseous emissions include:

- increasing the pH in the sludge thickener to 8.5;
- continuously drawing off the sludge;
- feeding certain waste water streams containing sulphur compounds to neutralisation using separate plunged pipes.

Applicability
The techniques are generally applicable. However, the minimisation of residence times may be restricted in the case of existing collection and treatment systems.

Economics
No information provided.

Driving force for implementation
The driving forces for the implementation of the techniques mentioned include:

- national legislation on odours (e.g. TA Luft in Germany);
- odour nuisances (especially from sludge treatment) in the case of nearby housing;
- occurrence of odorous substances from anaerobic reactors, especially when waste water contains high concentrations of sulphate, which is converted to sulphides.

Example plants
The techniques indicated are used in many WWTPs. Examples plants from Germany are mentioned above under 'operational data'. Ecologica Naviglio S.p.A. (central WWTP treating mainly waste waters originating from tanneries and the textile industry, but also other types of waste waters). Robecchetto con Induno (MI) in Italy uses covers for the treatment basins.

Reference literature
[103, COM 2007] [202, Capelli et al. 2009] [224, RP Freiburg 2009] [225, Schafer 1995]

3.5.5.4.2 End-of pipe treatment techniques

3.5.5.4.2.1 Overview

[104, COM 2003] [195, ADEME 2009] [196, ADEME 2005] [198, Schlegelmilch et al. 2005]

Several of the common treatment techniques described in Section 3.3 to treat non-odorous gaseous pollutants may also be used to prevent or abate/minimise odour emissions and the description of these techniques (an overview of which is presented in Table 3.304) will not be repeated in the following sections. Because many odorous compounds are VOC compounds, abatement operations and processes described in Sections 3.5.1.2 and 3.5.1.3 are of particular interest.

Very high abatement efficiencies are required for the treatment of odorous emissions as humans are sensitive to very low concentrations of certain odorous substances.

There are a number of parameters to consider for selecting treatment techniques to minimise odour emissions:

- the flow rate of the odorous emissions;
- the concentration of the odorous pollutant(s);
- the physical and chemical properties of the odorous molecules, such as solubility, acidity, basicity, polarity, adsorbability, biodegradability;
- the efficiency of the techniques to abate the targeted odorous pollutants and the variability over time of this abatement efficiency (especially when catalysts are used);
- the generation of secondary pollutants;
- the energy consumption of the techniques;
- the technical limits/restrictions for the use of the techniques (e.g. temperature, maximum pollutants concentration, moisture content);
- the space requirements of the techniques;
- the operation and maintenance requirements of the techniques;
- the costs of the techniques.

Table 3.304 provides an overview of end-of-pipe odour treatment techniques.

Table 3.304: Overview of end-of-pipe odour treatment techniques

Technique	Odour abatement efficiency ([1]) (%)	Section in the BREF	Comments
Adsorption	80–99	Section 3.5.1.2.3	—
Wet scrubbers	60–85	Section 3.5.1.2.4	—
Alkaline oxidative scrubbing	80–90	Section 3.5.5.4.2.2	Variant of the absorption technique
Thermal oxidation	98–99.9	Section 3.5.1.3.5	—
Catalytic oxidation	80–95	Section 3.5.1.3.6	—
Biofiltration ([2])	70–99	Section 3.5.1.3.1	Low shift of pollution to any other media. Few chemical agents added. Low energy consumption
Bioscrubbing ([2])	70–80	Section 3.5.1.3.2	—
Biotrickling	70–90	Section 3.5.1.3.3	—
Moving-bed trickling filter	> 90	Section 3.5.1.3.4	—
Ionisation	80–98	Section 3.5.1.3.7	—
Photo/UV oxidation	80–98	Section 3.5.1.3.8	—

([1]) As reported in the corresponding section of this document where the technique is described.
([2]) Biofiltration and bioscrubbing can be combined into one system to benefit from the advantages of both techniques. The bioscrubber would act as a humidifier and degrade a high portion of the odorous load. It will also display a buffering effect to prevent high concentrations of odorous substances from entering the biofilter, which otherwise might lead to a rise in temperature in the biofilter material due to an increasing degradation process [198, Schlegelmilch *et al.* 2005]. Elevated temperatures would result in a lower efficiency of the biofilter.

Measures taken to prevent fugitive/diffuse gaseous and liquid emissions (e.g. leak minimisation through proper design of storage and handling facilities, seals on pumps) are also beneficial with respect to odour problems. More information on these techniques can be found in the corresponding section of this document (see Section 3.5.4). However, many sulphur compounds have low or very low odour thresholds and conventional equipment designs (e.g. flanged pipework, centrifugal pumps) may have an unacceptable level of releases. This results in the use of all-welded pipework, canned pumps and scrubbing equipment [104, COM 2003].

3.5.5.4.2.2   Alkaline oxidative scrubber

Description
Alkaline oxidative gas scrubbing is a variant of wet gas scrubbing (see Section 3.5.1.2.4) which is mostly applied for odour control. The organic odorous compounds are oxidised in the alkaline environment at pH 7–10. Sodium hypochlorite (NaOCl), potassium permanganate ($KMnO_4$) or hydrogen peroxide (H_2O_2) are used as strong oxidants. When using potassium permanganate as an oxidant, MnO_2 is generated and has to be removed from the scrubbing liquid periodically. When sodium hypochlorite is used, chloride is formed while no side products are formed when using hydrogen peroxide. However, hydrogen peroxide is not as strong an oxidant as sodium hypochlorite and potassium permanganate. Especially for odour removal, it is recommended to test the technique on a smaller scale first to determine the specific removal efficiency. If amines are present in the incoming gases, it is recommended to use acid scrubbing (see Section 3.5.1.2.4 on wet scrubbers for gas removal) beforehand in order to prevent the forming of chloramines.

Achieved environmental benefits
Abatement efficiencies and emission levels associated with alkaline oxidative scrubbers are given in Table 3.305.

Table 3.305: Abatement efficiencies and emission levels associated with alkaline oxidative scrubbers

Pollutant	Abatement efficiency (%) ([1])	Emission level (mg/Nm^3) ([1])
Odour	80–90	Specific to the situation

([1]) Efficiency depends on the specific plant configuration, operational conditions and reagents used; the performances indicated are based upon half-hourly averages.

Source: [176, Schenk et al. 2009].

Comparative research for odour abatement efficiencies between scrubbers and biofilters (see Section 3.5.1.3.1) show that biofilters reach higher efficiencies [176, Schenk et al. 2009].

Cross-media effects
When using an alkaline oxidative scrubber with NaOCl, toxic chlorine fumes might be formed at low pH values. An alkaline scrubber might then be placed in series to the alkaline oxidative scrubber to remove these chlorine fumes. Consumables associated with alkaline oxidative scrubbers are given in Table 3.306.

Table 3.306: Consumables associated with alkaline oxidative scrubbers

Consumable	Amount	Comments
Scrubbing water	Strongly depends on the application	The consumption of water is dependent on the incoming and outgoing concentrations of gaseous compounds. Evaporation losses are primarily determined by the temperature and the air humidity of the incoming gas stream. The outgoing gas stream is, in most cases, completely saturated with water vapour
Caustic soda	NI	—
Chemical oxidants	NI	—
Energy (kWh/1 000 Nm^3/h)	0.2–1	Dependent on application, desorption not included
Pressure drop (mbar)	~ 12	Dependent on application

NB: NI = no information provided.
Source: [176, Schenk et al. 2009].

The dosing of the reagents should be automated in order to achieve a consistent performance and to minimise the use of reagents. The oxidant is dosed in slight excess.

Operational data
Design and maintenance [176, Schenk et al. 2009]
An optimally designed scrubbing system with low emissions requires high reliability, full automation and a good level of maintenance. The most important design parameters are gas flow, operational temperature, maximum temperature and waste gas composition. When designing an alkaline oxidative scrubbing system, synthetic material is used as the primary construction material.

The abatement efficiency depends on the oxidisability of the compounds and the residence time in the scrubber. An increase in the residence time requires larger installations and higher investment costs. Pilot tests are essential for achieving good design.

Monitoring [176, Schenk et al. 2009]
Monitoring aspects of scrubbers are described in Section 3.5.1.2.4. Odour measurements require a specific approach (see Section 3.5.5.3.1).

Applicability
Application limits and restrictions are given in Table 3.307.

Table 3.307: Application limits and restrictions associated with alkaline oxidative scrubbers

Issue	Limits/restrictions
Gas flow (Nm^3/h)	50–500 000
Temperature (°C)	5–80
Pressure	Atmospheric
Pressure drop (mbar)	~ 12
Particulates content (mg/Nm^3)	< 10
Source: [176, Schenk et al. 2009].	

Advantages and disadvantages are given in Table 3.308.

Table 3.308: Advantages and disadvantages associated with alkaline oxidative scrubbers

Advantages	Disadvantages
• Relatively high abatement efficiency can be reached for aromatic substances	• Use of strong oxidants requires some safety precautions and a special design of the installation

Economics
Economics associated with alkaline oxidative scrubbers are given in Table 3.309.

Table 3.309: Economics associated with alkaline oxidative scrubbers

Investment costs ($EUR/1 000\ Nm^3/h$)	10 000–35 000, strongly depends on the design
Operating costs: Labour (days/week)	About 0.5–1
Consumables/additives	Depending on the chemicals used
Cost-determining parameters	Flow, reagents and odorous compounds to be abated
Benefits	None
Source: [176, Schenk et al. 2009].	

Driving force for implementation
No information provided.

Example plants
Alkaline oxidative scrubbing is reported to be used in the sectors such as the food industry, slaughterhouses, flavouring agents production and the textiles industry.

Reference literature
[176, Schenk et al. 2009]

4 BEST AVAILABLE TECHNIQUES (BAT) CONCLUSIONS FOR COMMON WASTE WATER/WASTE GAS TREATMENT/MANAGEMENT SYSTEMS IN THE CHEMICAL SECTOR

SCOPE

These BAT conclusions concern the activities specified in Sections 4 and 6.11 of Annex I to Directive 2010/75/EU, namely:

- Section 4: Chemical industry;
- Section 6.11: Independently operated treatment of waste water not covered by Council Directive 91/271/EEC and discharged by an installation undertaking activities covered under Section 4 of Annex I to Directive 2010/75/EU.

These BAT conclusions also cover the combined treatment of waste water from different origins if the main pollutant load originates from the activities covered under Section 4 of Annex I to Directive 2010/75/EU.

In particular, these BAT conclusions cover the following issues:

- environmental management systems;
- water saving;
- waste water management, collection, and treatment;
- waste management;
- treatment of waste water sludge with the exception of incineration;
- waste gas management, collection, and treatment;
- flaring;
- diffuse emissions of volatile organic compounds (VOC) to air;
- odour emissions;
- noise emissions.

Other BAT conclusions and reference documents which could be relevant for the activities covered by these BAT conclusions are the following:

- Production of Chlor-alkali (CAK);
- Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers (LVIC-AAF);
- Manufacture of Large Volume Inorganic Chemicals – Solids and Others Industry (LVIC-S);
- Production of Speciality Inorganic Chemicals (SIC);
- Large Volume Organic Chemical Industry (LVOC);
- Manufacture of Organic Fine Chemicals (OFC);
- Production of Polymers (POL);
- Emissions from Storage (EFS);
- Energy Efficiency (ENE);
- Monitoring of Emissions to Air and Water from IED installations (ROM);
- Industrial Cooling Systems (ICS);
- Large Combustion Plants (LCP);
- Waste Incineration (WI);
- Waste Treatments Industries (WT);
- Economics and Cross-media Effects (ECM).

GENERAL CONSIDERATIONS

Best Available Techniques

The techniques listed and described in these BAT conclusions are neither prescriptive nor exhaustive. Other techniques may be used that ensure at least an equivalent level of environmental protection.

Unless otherwise stated, the BAT conclusions are generally applicable.

Emission levels associated with BAT

Emission levels associated with the best available techniques (BAT-AELs) for emissions to water given in these BAT conclusions refer to values of concentrations (mass of emitted substances per volume of water), expressed in µg/l or mg/l.

Unless otherwise stated, the BAT-AELs refer to flow-weighted yearly averages of 24-hour flow-proportional composite samples, taken with the minimum frequency set for the relevant parameter and under normal operating conditions. Time-proportional sampling can be used provided that sufficient flow stability is demonstrated.

The flow-weighted yearly average concentration of the parameter (c_w) is calculated using the following equation:

$$c_w = \sum_{i=1}^{n} c_i q_i \Bigg/ \sum_{i=1}^{n} q_i$$

Where

n = number of measurements;
c_i = average concentration of the parameter during i^{th} measurement;
q_i = average flow rate during i^{th} measurement.

Abatement efficiencies

In the case of total organic carbon (TOC), chemical oxygen demand (COD), total nitrogen (TN) and total inorganic nitrogen (N_{inorg}), the calculation of the average abatement efficiency referred to in these BAT conclusions (see Table 4.1 and Table 4.2) is based on loads and includes both pretreatment (BAT 10 c) and final treatment (BAT 10 d) of waste water.

DEFINITIONS

For the purposes of these BAT conclusions, the following definitions apply:

Term used	Definition
New plant	A plant first permitted at the site of the installation following the publication of these BAT conclusions or a complete replacement of a plant following the publication of these BAT conclusions.
Existing plant	A plant that is not a new plant.
Biochemical oxygen demand (BOD_5)	Amount of oxygen needed for the biochemical oxidation of the organic matter to carbon dioxide in 5 days. BOD is an indicator for the mass concentration of biodegradable organic compounds.
Chemical oxygen demand (COD)	Amount of oxygen needed for the total oxidation of the organic matter to carbon dioxide. COD is an indicator for the mass concentration of organic compounds.
Total organic carbon (TOC)	Total organic carbon, expressed as C, includes all organic compounds.
Total suspended solids (TSS)	Mass concentration of all suspended solids, measured via filtration through glass fibre filters and gravimetry.
Total nitrogen (TN)	Total nitrogen, expressed as N, includes free ammonia and ammonium (NH_4-N), nitrites (NO_2-N), nitrates (NO_3-N) and organic nitrogen compounds.
Total inorganic nitrogen (N_{inorg})	Total inorganic nitrogen, expressed as N, includes free ammonia and ammonium (NH_4-N), nitrites (NO_2-N) and nitrates (NO_3-N).
Total phosphorus (TP)	Total phosphorus, expressed as P, includes all inorganic and organic phosphorus compounds, dissolved or bound to particles.
Adsorbable organically bound halogens (AOX)	Adsorbable organically bound halogens, expressed as Cl, include adsorbable organically bound chlorine, bromine and iodine.
Chromium (Cr)	Chromium, expressed as Cr, includes all inorganic and organic chromium compounds, dissolved or bound to particles.
Copper (Cu)	Copper, expressed as Cu, includes all inorganic and organic copper compounds, dissolved or bound to particles.
Nickel (Ni)	Nickel, expressed as Ni, includes all inorganic and organic nickel compounds, dissolved or bound to particles.
Zinc (Zn)	Zinc, expressed as Zn, includes all inorganic and organic zinc compounds, dissolved or bound to particles.
VOC	Volatile organic compounds as defined in Article 3(45) of Directive 2010/75/EU.
Diffuse VOC emissions	Non-channelled VOC emissions which can result from 'area' sources (e.g. tanks) or 'point' sources (e.g. pipe flanges).
Fugitive VOC emissions	Diffuse VOC emissions from 'point' sources.
Flaring	High-temperature oxidation to burn combustible compounds of waste gases from industrial operations with an open flame. Flaring is primarily used for burning off flammable gas for safety reasons or during non-routine operational conditions.

4.1   Environmental management systems

BAT 1.   In order to improve the overall environmental performance, BAT is to implement and adhere to an environmental management system (EMS) that incorporates all of the following features:

I.   commitment of the management, including senior management;
II.   an environmental policy that includes the continuous improvement of the installation by the management;
III.   planning and establishing the necessary procedures, objectives and targets, in conjunction with financial planning and investment;
IV.   implementation of procedures paying particular attention to:

    (a)   structure and responsibility;
    (b)   recruitment, training, awareness and competence;
    (c)   communication;
    (d)   employee involvement;
    (e)   documentation;
    (f)   effective process control;
    (g)   maintenance programmes;
    (h)   emergency preparedness and response;
    (i)   safeguarding compliance with environmental legislation;

V.   checking performance and taking corrective action, paying particular attention to:

    (a)   monitoring and measurement (see also the Reference Report on Monitoring of Emissions to Air and Water from IED installations – ROM);
    (b)   corrective and preventive action;
    (c)   maintenance of records;
    (d)   independent (where practicable) internal or external auditing in order to determine whether or not the EMS conforms to planned arrangements and has been properly implemented and maintained;

VI.   review of the EMS and its continuing suitability, adequacy and effectiveness by senior management;
VII.   following the development of cleaner technologies;
VIII.   consideration for the environmental impacts from the eventual decommissioning of the plant at the design stage of a new plant, and throughout its operating life;
IX.   application of sectoral benchmarking on a regular basis;
X.   waste management plan (see BAT 13).

Specifically for chemical sector activities, BAT is to incorporate the following features in the EMS:

XI.   on multi-operator installations/sites, establishment of a convention that sets out the roles, responsibilities and coordination of operating procedures of each plant operator in order to enhance the cooperation between the various operators;
XII.   establishment of inventories of waste water and waste gas streams (see BAT 2).

In some cases, the following features are part of the EMS:

XIII.   odour management plan (see BAT 20);
XIV.   noise management plan (see BAT 22).

Applicability

The scope (e.g. level of detail) and nature of the EMS (e.g. standardised or non-standardised) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have.

BAT 2.   In order to facilitate the reduction of emissions to water and air and the reduction of water usage, BAT is to establish and to maintain an inventory of waste water and waste gas streams, as part of the environmental management system (see BAT 1), that incorporates all of the following features:

I.   information about the chemical production processes, including:

    (a) chemical reaction equations, also showing side products;
    (b) simplified process flow sheets that show the origin of the emissions;
    (c) descriptions of process-integrated techniques and waste water/waste gas treatment at source including their performances;

II.   information, as comprehensive as is reasonably possible, about the characteristics of the waste water streams, such as:

    (a) average values and variability of flow, pH, temperature, and conductivity;
    (b) average concentration and load values of relevant pollutants/parameters and their variability (e.g. COD/TOC, nitrogen species, phosphorus, metals, salts, specific organic compounds);
    (c) data on bioeliminability (e.g. BOD, BOD/COD ratio, Zahn-Wellens test, biological inhibition potential (e.g. nitrification));

III.   information, as comprehensive as is reasonably possible, about the characteristics of the waste gas streams, such as:

    (a) average values and variability of flow and temperature;
    (b) average concentration and load values of relevant pollutants/parameters and their variability (e.g. VOC, CO, NO_X, SO_X, chlorine, hydrogen chloride);
    (c) flammability, lower and higher explosive limits, reactivity;
    (d) presence of other substances that may affect the waste gas treatment system or plant safety (e.g. oxygen, nitrogen, water vapour, dust).

4.2 Monitoring

BAT 3. **For relevant emissions to water as identified by the inventory of waste water streams (see BAT 2), BAT is to monitor key process parameters (including continuous monitoring of waste water flow, pH and temperature) at key locations (e.g. influent to pretreatment and influent to final treatment).**

BAT 4. **BAT is to monitor emissions to water in accordance with EN standards with at least the minimum frequency given below. If EN standards are not available, BAT is to use ISO, national or other international standards that ensure the provision of data of an equivalent scientific quality.**

Substance/parameter		Standard(s)	Minimum monitoring frequency ([1]) ([2])
Total organic carbon (TOC) ([3])		EN 1484	Daily
Chemical oxygen demand (COD) ([3])		No EN standard available	
Total suspended solids (TSS)		EN 872	
Total nitrogen (TN) ([4])		EN 12260	
Total inorganic nitrogen (N_{inorg}) ([4])		Various EN standards available	
Total phosphorus (TP)		Various EN standards available	
Adsorbable organically bound halogens (AOX)		EN ISO 9562	Monthly
Metals	Cr	Various EN standards available	
	Cu		
	Ni		
	Pb		
	Zn		
	Other metals, if relevant		
Toxicity ([5])	Fish eggs (*Danio rerio*)	EN ISO 15088	To be decided based on a risk assessment, after an initial characterisation
	Daphnia (*Daphnia magna Straus*)	EN ISO 6341	
	Luminescent bacteria (*Vibrio fischeri*)	EN ISO 11348–1, EN ISO 11348–2 or EN ISO 11348–3	
	Duckweed (*Lemna minor*)	EN ISO 20079	
	Algae	EN ISO 8692, EN ISO 10253 or EN ISO 10710	

([1]) Monitoring frequencies may be adapted if the data series clearly demonstrate a sufficient stability.
([2]) The sampling point is located where the emission leaves the installation.
([3]) TOC monitoring and COD monitoring are alternatives. TOC monitoring is the preferred option because it does not rely on the use of very toxic compounds.
([4]) TN and N_{inorg} monitoring are alternatives.
([5]) An appropriate combination of these methods can be used.

BAT 5. **BAT is to periodically monitor diffuse VOC emissions to air from relevant sources by using an appropriate combination of the techniques I – III or, where large amounts of VOC are handled, all of the techniques I – III.**

I. sniffing methods (e.g. with portable instruments according to EN 15446) associated with correlation curves for key equipment;
II. optical gas imaging methods;
III. calculation of emissions based on emissions factors, periodically validated (e.g. once every two years) by measurements.

Where large amounts of VOCs are handled, the screening and quantification of emissions from the installation by periodic campaigns with optical absorption-based techniques, such as Differential absorption light detection and ranging (DIAL) or Solar occultation flux (SOF), is a useful complementary technique to the techniques I to III.

Description
See Section 4.6.2.

BAT 6.   BAT is to periodically monitor odour emissions from relevant sources in accordance with EN standards.

Description
Emissions can be monitored by dynamic olfactometry according to EN 13725. Emission monitoring may be complemented by measurement/estimation of odour exposure or estimation of odour impact.

Applicability
The applicability is restricted to cases where odour nuisance can be expected or has been substantiated.

4.3   Emissions to water

4.3.1   Water usage and waste water generation

BAT 7.   In order to reduce the usage of water and the generation of waste water, BAT is to reduce the volume and/or pollutant load of waste water streams, to enhance the reuse of waste water within the production process and to recover and reuse raw materials.

4.3.2   Waste water collection and segregation

BAT 8.   In order to prevent the contamination of uncontaminated water and to reduce emissions to water, BAT is to segregate uncontaminated waste water streams from waste water streams that require treatment.

Applicability
The segregation of uncontaminated rainwater may not be applicable in the case of existing waste water collection systems.

BAT 9.   In order to prevent uncontrolled emissions to water, BAT is to provide an appropriate buffer storage capacity for waste water incurred during other than normal operating conditions based on a risk assessment (taking into account e.g. the nature of the pollutant, the effects on further treatment, and the receiving environment), and to take appropriate further measures (e.g. control, treat, reuse).

Applicability
The interim storage of contaminated rainwater requires segregation, which may not be applicable in the case of existing waste water collection systems.

4.3.3   Waste water treatment

BAT 10.   In order to reduce emissions to water, BAT is to use an integrated waste water management and treatment strategy that includes an appropriate combination of the techniques in the priority order given below.

	Technique	Description
a	Process-integrated techniques ([1])	Techniques to prevent or reduce the generation of water pollutants.
b	Recovery of pollutants at source ([1])	Techniques to recover pollutants prior to their discharge to the waste water collection system.
c	Waste water pretreatment ([1]) ([2])	Techniques to abate pollutants before the final waste water treatment. Pretreatment can be carried out at the source or in combined streams.
d	Final waste water treatment ([3])	Final waste water treatment by, for example, preliminary and primary treatment, biological treatment, nitrogen removal, phosphorus removal and/or final solids removal techniques before discharge to a receiving water body.
([1]) These techniques are further described and defined in other BAT conclusions for the chemical industry. ([2]) See BAT 11. ([3]) See BAT 12.		

Description

The integrated waste water management and treatment strategy is based on the inventory of waste water streams (see BAT 2).

BAT-associated emission levels (BAT-AELs): See Section 4.3.4.

BAT 11.   In order to reduce emissions to water, BAT is to pretreat waste water that contains pollutants that cannot be dealt with adequately during final waste water treatment by using appropriate techniques.

Description

Waste water pretreatment is carried out as part of an integrated waste water management and treatment strategy (see BAT 10) and is generally necessary to:

- protect the final waste water treatment plant (e.g. protection of a biological treatment plant against inhibitory or toxic compounds);
- remove compounds that are insufficiently abated during final treatment (e.g. toxic compounds, poorly/non-biodegradable organic compounds, organic compounds that are present in high concentrations, or metals during biological treatment);
- remove compounds that are otherwise stripped to air from the collection system or during final treatment (e.g. volatile halogenated organic compounds, benzene);
- remove compounds that have other negative effects (e.g. corrosion of equipment; unwanted reaction with other substances; contamination of waste water sludge).

In general, pretreatment is carried out as close as possible to the source in order to avoid dilution, in particular for metals. Sometimes, waste water streams with appropriate characteristics can be segregated and collected in order to undergo a dedicated combined pretreatment.

BAT 12.   In order to reduce emissions to water, BAT is to use an appropriate combination of final waste water treatment techniques.

Description

Final waste water treatment is carried out as part of an integrated waste water management and treatment strategy (see BAT 10).

Appropriate final waste water treatment techniques, depending on the pollutant, include:

	Technique ([1])	Typical pollutants abated	Applicability
Preliminary and primary treatment			
a	Equalisation	All pollutants	Generally applicable.
b	Neutralisation	Acids, alkalis	
c	Physical separation, e.g. screens, sieves, grit separators, grease separators or primary settlement tanks	Suspended solids, oil/grease	
Biological treatment (secondary treatment), e.g.			
d	Activated sludge process	Biodegradable organic compounds	Generally applicable.
e	Membrane bioreactor		
Nitrogen removal			
f	Nitrification/denitrification	Total nitrogen, ammonia	Nitrification may not be applicable in case of high chloride concentrations (i.e. around 10 g/l) and provided that the reduction of the chloride concentration prior to nitrification would not be justified by the environmental benefits. Not applicable when the final treatment does not include a biological treatment.
Phosphorus removal			
g	Chemical precipitation	Phosphorus	Generally applicable.
Final solids removal			
h	Coagulation and flocculation	Suspended solids	Generally applicable.
i	Sedimentation		
j	Filtration (e.g. sand filtration, microfiltration, ultrafiltration)		
k	Flotation		
([1]) The descriptions of the techniques are given in Section 4.6.1			

4.3.4   BAT-associated emission levels for emissions to water

The BAT-associated emission levels (BAT-AELs) for emissions to water given in Table 4.1, Table 4.2 and Table 4.3 apply to direct emissions to a receiving water body from:

(i)   the activities specified in Section 4 of Annex I to Directive 2010/75/EU;

(ii) independently operated waste water treatment plants specified in Section 6.11 of Annex I to Directive 2010/75/EU provided that the main pollutant load originates from activities specified in Section 4 of Annex I to Directive 2010/75/EU;

(iii) the combined treatment of waste water from different origins provided that the main pollutant load originates from activities specified in Section 4 of Annex I to Directive 2010/75/EU.

The BAT-AELs apply at the point where the emission leaves the installation.

Table 4.1:   BAT-AELs for direct emissions of TOC, COD, and TSS to a receiving water body

Parameter	BAT-AEL (yearly average)	Conditions
Total organic carbon (TOC) ([1]) ([2])	10–33 mg/l ([3]) ([4]) ([5]) ([6])	The BAT-AEL applies if the emission exceeds 3.3 t/yr.
Chemical oxygen demand (COD) ([1]) ([2])	30–100 mg/l ([3]) ([4]) ([5]) ([6])	The BAT-AEL applies if the emission exceeds 10 t/yr.
Total suspended solids (TSS)	5.0–35 mg/l ([7]) ([8])	The BAT-AEL applies if the emission exceeds 3.5 t/yr.

([1])   No BAT-AEL applies for biochemical oxygen demand (BOD). As an indication, the yearly average BOD_5 level in the effluent from a biological waste water treatment plant will generally be ≤ 20 mg/l.

([2])   Either the BAT-AEL for TOC or the BAT-AEL for COD applies. TOC is the preferred option because its monitoring does not rely on the use of very toxic compounds.

([3])   The lower end of the range is typically achieved when few tributary waste water streams contain organic compounds and/or the waste water mostly contains easily biodegradable organic compounds.

([4])   The upper end of the range may be up to 100 mg/l for TOC or up to 300 mg/l for COD, both as yearly averages, if both of the following conditions are fulfilled:
- Condition A: Abatement efficiency $\geq 90\%$ as a yearly average (including both pretreatment and final treatment).
- Condition B: If a biological treatment is used, at least one of the following criteria is met:
  - A low-loaded biological treatment step is used (i.e. ≤ 0.25 kg COD/kg of organic dry matter of sludge). This implies that the BOD_5 level in the effluent is ≤ 20 mg/l.
  - Nitrification is used.

([5])   The upper end of the range may not apply if all of the following conditions are fulfilled:
- Condition A: Abatement efficiency $\geq 95\%$ as a yearly average (including both pretreatment and final treatment).
- Condition B: same as Condition B in footnote ([4]).
- Condition C: The influent to the final waste water treatment shows the following characteristics: TOC > 2 g/l (or COD > 6 g/l) as a yearly average and a high proportion of refractory organic compounds.

([6])   The upper end of the range may not apply when the main pollutant load originates from the production of methylcellulose.

([7])   The lower end of the range is typically achieved when using filtration (e.g. sand filtration, microfiltration, ultrafiltration, membrane bioreactor), while the upper end of the range is typically achieved when using sedimentation only.

([8])   This BAT-AEL may not apply when the main pollutant load originates from the production of soda ash via the Solvay process or from the production of titanium dioxide.

Table 4.2:   BAT-AELs for direct emissions of nutrients to a receiving water body

Parameter	BAT-AEL (yearly average)	Conditions
Total nitrogen (TN) ([1])	5.0–25 mg/l ([2]) ([3])	The BAT-AEL applies if the emission exceeds 2.5 t/yr.
Total inorganic nitrogen (N_{inorg}) ([1])	5.0–20 mg/l ([2]) ([3])	The BAT-AEL applies if the emission exceeds 2.0 t/yr.
Total phosphorus (TP)	0.50–3.0 mg/l ([4])	The BAT-AEL applies if the emission exceeds 300 kg/yr.

([1])   Either the BAT-AEL for total nitrogen or the BAT-AEL for total inorganic nitrogen applies.

([2])   The BAT-AELs for TN and N_{inorg} do not apply to installations without biological waste water treatment. The lower end of the range is typically achieved when the influent to the biological waste water treatment plant contains low levels of nitrogen and/or when nitrification/denitrification can be operated under optimum conditions.

([3])   The upper end of the range may be higher and up to 40 mg/l for TN or 35 mg/l for N_{inorg}, both as yearly averages, if the abatement efficiency is $\geq 70\%$ as a yearly average (including both pretreatment and final treatment).

([4])   The lower end of the range is typically achieved when phosphorus is added for the proper operation of the biological waste water treatment plant or when phosphorus mainly originates from heating or cooling systems. The upper end of the range is typically achieved when phosphorus-containing compounds are produced by the installation.

Table 4.3:   BAT-AELs for direct emissions of AOX and metals to a receiving water body

Parameter	BAT-AEL (yearly average)	Conditions
Adsorbable organically bound halogens (AOX)	0.20–1.0 mg/l ([1]) ([2])	The BAT-AEL applies if the emission exceeds 100 kg/yr.
Chromium (expressed as Cr)	5.0–25 µg/l ([3]) ([4]) ([5]) ([6])	The BAT-AEL applies if the emission exceeds 2.5 kg/yr.
Copper (expressed as Cu)	5.0–50 µg/l ([3]) ([4]) ([5]) ([7])	The BAT-AEL applies if the emission exceeds 5.0 kg/yr.
Nickel (expressed as Ni)	5.0–50 µg/l ([3]) ([4]) ([5])	The BAT-AEL applies if the emission exceeds 5.0 kg/yr.
Zinc (expressed as Zn)	20–300 µg/l ([3]) ([4]) ([5]) ([8])	The BAT-AEL applies if the emission exceeds 30 kg/yr.

([1])   The lower end of the range is typically achieved when few halogenated organic compounds are used or produced by the installation.
([2])   This BAT-AEL may not apply when the main pollutant load originates from the production of iodinated X-ray contrast agents due to the high refractory loads. This BAT-AEL may also not apply when the main pollutant load originates from the production of propylene oxide or epichlorohydrin via the chlorohydrin process due to the high loads.
([3])   The lower end of the range is typically achieved when few of the corresponding metal (compounds) are used or produced by the installation.
([4])   This BAT-AEL may not apply to inorganic effluents when the main pollutant load originates from the production of inorganic heavy metal compounds.
([5])   This BAT-AEL may not apply when the main pollutant load originates from the processing of large volumes of solid inorganic raw materials that are contaminated with metals (e.g. soda ash from the Solvay process, titanium dioxide).
([6])   This BAT-AEL may not apply when the main pollutant load originates from the production of chromium-organic compounds.
([7])   This BAT-AEL may not apply when the main pollutant load originates from the production of copper-organic compounds or the production of vinyl chloride monomer/ethylene dichloride via the oxychlorination process.
([8])   This BAT-AEL may not apply when the main pollutant load originates from the production of viscose fibres.

The associated monitoring is in BAT 4.

4.4   Waste

BAT 13.   In order to prevent or, where this is not practicable, to reduce the quantity of waste being sent for disposal, BAT is to set up and implement a waste management plan as part of the environmental management system (see BAT 1) that, in order of priority, ensures that waste is prevented, prepared for reuse, recycled or otherwise recovered.

BAT 14.   In order to reduce the volume of waste water sludge requiring further treatment or disposal, and to reduce its potential environmental impact, BAT is to use one or a combination of the techniques given below.

	Technique	Description	Applicability
a	Conditioning	Chemical conditioning (i.e. adding coagulants and/or flocculants) or thermal conditioning (i.e. heating) to improve the conditions during sludge thickening/dewatering.	Not applicable to inorganic sludges. The necessity for conditioning depends on the sludge properties and on the thickening/dewatering equipment used.
b	Thickening/dewatering	Thickening can be carried out by sedimentation, centrifugation, flotation, gravity belts, or rotary drums. Dewatering can be carried out by belt filter presses or plate filter presses.	Generally applicable.
c	Stabilisation	Sludge stabilisation includes chemical treatment, thermal treatment, aerobic digestion, or anaerobic digestion.	Not applicable to inorganic sludges. Not applicable for short-term handling before final treatment.
d	Drying	Sludge is dried by direct or indirect contact with a heat source.	Not applicable to cases where waste heat is not available or cannot be used.

4.5 Emissions to air

4.5.1 Waste gas collection

BAT 15.   In order to facilitate the recovery of compounds and the reduction of emissions to air, BAT is to enclose the emission sources and to treat the emissions, where possible.

Applicability
The applicability may be restricted by concerns on operability (access to equipment), safety (avoiding concentrations close to the lower explosive limit) and health (where operator access is required inside the enclosure).

4.5.2 Waste gas treatment

BAT 16.   In order to reduce emissions to air, BAT is to use an integrated waste gas management and treatment strategy that includes process-integrated and waste gas treatment techniques.

Description
The integrated waste gas management and treatment strategy is based on the inventory of waste gas streams (see BAT 2) giving priority to process-integrated techniques.

4.5.3 Flaring

BAT 17.   In order to prevent emissions to air from flares, BAT is to use flaring only for safety reasons or non-routine operational conditions (e.g. start-ups, shutdowns) by using one or both of the techniques given below.

	Technique	Description	Applicability
a	Correct plant design	This includes the provision of a gas recovery system with sufficient capacity and the use of high-integrity relief valves.	Generally applicable to new plants. Gas recovery systems may be retrofitted in existing plants.
b	Plant management	This includes balancing the fuel gas system and using advanced process control.	Generally applicable.

BAT 18.   In order to reduce emissions to air from flares when flaring is unavoidable, BAT is to use one or both of the techniques given below.

	Technique	Description	Applicability
a	Correct design of flaring devices	Optimisation of height, pressure, assistance by steam, air or gas, type of flare tips (either enclosed or shielded), etc., aimed to enable smokeless and reliable operation and to ensure the efficient combustion of excess gases.	Applicable to new flares. In existing plants, applicability may be restricted due to e.g. maintenance time availability during the turnaround of the plant.
b	Monitoring and recording as part of flare management	Continuous monitoring of the gas sent to flaring, measurements of gas flow and estimations of other parameters (e.g. composition, heat content, ratio of assistance, velocity, purge gas flow rate, pollutant emissions (e.g. NO_X, CO, hydrocarbons, noise)). The recording of flaring events usually includes the estimated/measured flare gas composition, the estimated/measured flare gas quantity and the duration of operation. The recording allows for the quantification of emissions and the potential prevention of future flaring events.	Generally applicable.

4.5.4   Diffuse VOC emissions

BAT 19.   In order to prevent or, where that is not practicable, to reduce diffuse VOC emissions to air, BAT is to use a combination of the techniques given below.

	Technique	Applicability
Techniques related to plant design		
a	Limit the number of potential emission sources	Applicability may be restricted in the case of existing plants due to operability requirements.
b	Maximise process-inherent containment features	
c	Select high-integrity equipment (see the description in Section 4.6.2)	
d	Facilitate maintenance activities by ensuring access to potentially leaky equipment	
Techniques related to plant/equipment construction, assembly and commissioning		
e	Ensure well-defined and comprehensive procedures for plant/equipment construction and assembly. This includes using the designed gasket stress for flanged joint assembly (see the description in Section 4.6.2)	Generally applicable.
f	Ensure robust plant/equipment commissioning and handover procedures in line with the design requirements	
Techniques related to plant operation		
g	Ensure good maintenance and timely replacement of equipment	Generally applicable.
h	Use a risk-based leak detection and repair (LDAR) programme (see the description in Section 4.6.2)	
i	As far as it is reasonable, prevent diffuse VOC emissions, collect them at source, and treat them	

The associated monitoring is in BAT 5.

4.5.5   Odour emissions

BAT 20.   In order to prevent or, where that is not practicable, to reduce odour emissions, BAT is to set up, implement and regularly review an odour management plan, as part of the environmental management system (see BAT 1), that includes all of the following elements:

I.   a protocol containing appropriate actions and timelines;
II.   a protocol for conducting odour monitoring;
III.   a protocol for response to identified odour incidents;
IV.   an odour prevention and reduction programme designed to identify the source(s), to measure/estimate odour exposure, to characterise the contributions of the sources, and to implement prevention and/or reduction measures.

The associated monitoring is in BAT 6.

Applicability
The applicability is restricted to cases where odour nuisance can be expected or has been substantiated.

BAT 21.   In order to prevent or, where that is not practicable, to reduce odour emissions from waste water collection and treatment and from sludge treatment, BAT is to use one or a combination of the techniques given below.

	Technique	Description	Applicability
a	Minimise residence times	Minimise the residence time of waste water and sludge in collection and storage systems, in particular under anaerobic conditions.	Applicability may be restricted in the case of existing collection and storage systems.
b	Chemical treatment	Use chemicals to destroy or to reduce the formation of odorous compounds (e.g. oxidation or precipitation of hydrogen sulphide).	Generally applicable.
c	Optimise aerobic treatment	This can include: i. controlling the oxygen content; ii. frequent maintenance of the aeration system; iii. use of pure oxygen; iv. removal of scum in tanks.	Generally applicable.
d	Enclosure	Cover or enclose facilities for collecting and treating waste water and sludge to collect the odorous waste gas for further treatment.	Generally applicable.
e	End-of-pipe treatment	This can include: i. biological treatment; ii. thermal oxidation.	Biological treatment is only applicable to compounds that are easily soluble in water and readily bioeliminable.

4.5.6   Noise emissions

BAT 22.   In order to prevent or, where that is not practicable, to reduce noise emissions, BAT is to set up and implement a noise management plan, as part of the environmental management system (see BAT 1), that includes all of the following elements:

I.   a protocol containing appropriate actions and timelines;
II.   a protocol for conducting noise monitoring;
III.   a protocol for response to identified noise incidents;
IV.   a noise prevention and reduction programme designed to identify the source(s), to measure/estimate noise exposure, to characterise the contributions of the sources and to implement prevention and/or reduction measures.

Applicability
The applicability is restricted to cases where noise nuisance can be expected or has been substantiated.

BAT 23.   In order to prevent or, where that is not practicable, to reduce noise emissions, BAT is to use one or a combination of the techniques given below.

	Technique	Description	Applicability
a	Appropriate location of equipment and buildings	Increasing the distance between the emitter and the receiver and using buildings as noise screens.	For existing plants, the relocation of equipment may be restricted by a lack of space or excessive costs.
b	Operational measures	This includes: i. improved inspection and maintenance of equipment; ii. closing of doors and windows of enclosed areas, if possible; iii. equipment operation by experienced staff; iv. avoidance of noisy activities at night, if possible; v. provisions for noise control during maintenance activities.	Generally applicable.
c	Low-noise equipment	This includes low-noise compressors, pumps and flares.	Applicable only when the equipment is new or replaced.
d	Noise-control equipment	This includes: i. noise-reducers; ii. equipment insulation; iii. enclosure of noisy equipment; iv. soundproofing of buildings.	Applicability may be restricted due to space requirements (for existing plants), health, and safety issues.
e	Noise abatement	Inserting obstacles between emitters and receivers (e.g. protection walls, embankments and buildings).	Applicable only to existing plants, since the design of new plants should make this technique unnecessary. For existing plants, the insertion of obstacles may be restricted by a lack of space.

4.6   Descriptions of techniques

4.6.1   Waste water treatment

Technique	Description
Activated sludge process	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 mineralised into carbon dioxide and water or are transformed into other metabolites and biomass (i.e. the activated sludge). The microorganisms are maintained in suspension in the waste water and the whole mixture is mechanically aerated. The activated sludge mixture is sent to a separation facility from which the sludge is recycled to the aeration tank.
Nitrification/denitrification	A two-step process that is typically incorporated into biological waste water treatment plants. The first step is the aerobic nitrification where microorganisms oxidise ammonium (NH_4^+) to the intermediate nitrite (NO_2^-), which is then further oxidised to nitrate (NO_3^-). In the subsequent anoxic denitrification step, microorganisms chemically reduce nitrate to nitrogen gas.
Chemical precipitation	The conversion of dissolved pollutants into an insoluble compound by adding chemical precipitants. The solid precipitates formed are subsequently separated by sedimentation, air flotation, or filtration. If necessary, this may be followed by microfiltration or ultrafiltration. Multivalent metal ions (e.g. calcium, aluminium, iron) are used for phosphorus precipitation.
Coagulation and flocculation	Coagulation and flocculation are used to separate suspended solids from waste water and are often carried out in successive steps. Coagulation is carried out by adding coagulants with charges opposite to those of the suspended solids. Flocculation is carried out by adding polymers, so that collisions of microfloc particles cause them to bond to produce larger flocs.
Equalisation	Balancing of flows and pollutant loads at the inlet of the final waste water treatment by using central tanks. Equalisation may be decentralised or carried out using other management techniques.
Filtration	The separation of solids from waste water by passing them through a porous medium e.g. sand filtration, microfiltration and ultrafiltration.
Flotation	The separation of solid or liquid particles from waste water by attaching them to fine gas bubbles, usually air. The buoyant particles accumulate at the water surface and are collected with skimmers.
Membrane bioreactor	A combination of activated sludge treatment and membrane filtration. Two variants are used: a) an external recirculation loop between the activated sludge tank and the membrane module; and b) immersion of the membrane module into the aerated activated sludge tank, where the effluent is filtered through a hollow fibre membrane, the biomass remaining in the tank (this variant is less energy-consuming and results in more compact plants).
Neutralisation	The adjustment of the pH of waste water to a neutral level (approximately 7) by the addition of chemicals. Sodium hydroxide (NaOH) or calcium hydroxide ($Ca(OH)_2$) is generally used to increase the pH; whereas, sulphuric acid (H_2SO_4), hydrochloric acid (HCl) or carbon dioxide (CO_2) is generally used to decrease the pH. The precipitation of some substances may occur during neutralisation.
Sedimentation	The separation of suspended particles and suspended material by gravitational settling.

4.6.2 Diffuse VOC emissions

Technique	Description
High-integrity equipment	High-integrity equipment includes: - valves with double packing seals; - magnetically driven pumps/compressors/agitators; - pumps/compressors/agitators fitted with mechanical seals instead of packing; - high-integrity gaskets (such as spiral wound, ring joints) for critical applications; - corrosion-resistant equipment.
Leak detection and repair (LDAR) programme	A structured approach to reduce fugitive VOC emissions by detection and subsequent repair or replacement of leaking components. Currently, sniffing (described by EN 15446) and optical gas imaging methods are available for the identification of leaks. **Sniffing method**: The first step is the detection using hand-held VOC analysers measuring the concentration adjacent to the equipment (e.g. by using flame ionisation or photo-ionisation). The second step consists of bagging the component to carry out a direct measurement at the source of emission. This second step is sometimes replaced by mathematical correlation curves derived from statistical results obtained from a large number of previous measurements made on similar components. **Optical gas imaging methods**: Optical imaging uses small lightweight hand-held cameras which enable the visualisation of gas leaks in real time, so that they appear as 'smoke' on a video recorder together with the normal image of the component concerned, to easily and rapidly locate significant VOC leaks. Active systems produce an image with a back-scattered infrared laser light reflected on the component and its surroundings. Passive systems are based on the natural infrared radiation of the equipment and its surroundings.
Thermal oxidation	The oxidation of combustible gases and odorants in a waste gas stream by heating the mixture of contaminants with air or oxygen to above its auto-ignition point in a combustion chamber and maintaining it at a high temperature long enough to complete its combustion to carbon dioxide and water. Thermal oxidation is also referred to as 'incineration', 'thermal incineration' or 'oxidative combustion'.

Using the designed gasket stress for flanged joint assembly	This includes:
	  i. obtaining a certified high quality gasket, e.g. according to EN 13555;
	  ii. calculating the highest possible bolt load, e.g. according to EN 1591–1;
	  iii. obtaining a qualified flange-assembling equipment;
	  iv. supervision of the bolt tightening by a qualified fitter.

VOC diffuse emissions monitoring	Sniffing and optical gas imaging methods are described under leak detection and repair programme. Full screening and quantification of emissions from the installation can be undertaken with an appropriate combination of complementary methods, e.g. Solar occultation flux (SOF) or Differential absorption LIDAR (DIAL) campaigns. These results can be used for trend evaluation in time, cross-checking and updating/validation of the on-going LDAR programme. **Solar occultation flux (SOF)**: The technique is based on the recording and spectrometric Fourier Transform analysis of a broadband infrared or ultraviolet/visible sunlight spectra along a given geographical itinerary, crossing the wind direction and cutting through VOC plumes. **Differential absorption LIDAR (DIAL)**: This is a laser-based technique using differential absorption LIDAR (light detection and ranging), which is the optical analogue of radio wave-based RADAR. The technique relies on the back-scattering of laser beam pulses by atmospheric aerosols, and the analysis of spectral properties of the returned light collected with a telescope.

5 EMERGING TECHNIQUES

5.1 Waste water treatment techniques

5.1.1 Removal of sulphate and other pollutants using ultrasonic reactors

Description
Sulphate-rich waste waters are treated using the following process steps:

1. Reaction of the sulphate in the water effluent with aluminium hydroxide chloride under acidic conditions (ideally with pH < 1.3). The quantity of aluminium hydroxide chloride that is required is proportional to the concentration of sulphate within the effluent.
2. Neutralisation with lime slurry or liquid lime (the optimum pH has been found to be 11.5).
3. Treatment in an ultrasonic reactor at a controlled rate where sulphate can precipitate. The amplitude and power of the ultrasonic vibrations are controlled to optimise the efficiency of sulphate removal. Within the ultrasonic reactor, the reaction chemistry and kinetics are altered so that calcium aluminium sulphate oxide is formed. This material is a very fine precipitate, almost colloidal in nature, and it has been found that flocculation is started by the addition of Epofloc L1-R (a heavy metal precipitant which is a carbamine). Not only does this ensure the removal of any heavy metals that are present, it also removes any excess aluminium. The material is flocculated using an anionic polyacrylamide. The resultant supernatant is clear and colourless. The precipitant produced in the process has been analysed using x-ray fluorescence and diffraction and has been identified as a type of zeolite.
4. Clarification where sludge is removed and treated in a filter press and can then be disposed of or reused/recycled.

The technique can be applied as an end-of-pipe technique or included within a waste water treatment plant. An example of this is within a treatment plant, e.g. for chromium removal.

Achieved environmental benefits
The technique is used to remove the following contaminants from waste waters:

*   sulphate (up to 99.7 % reduction);
*   COD (up to 55 % reduction);
*   phosphate (up to 99.9 % reduction);
*   heavy metals (up to 99.7 % reduction).

The resultant filter cake produced has a lower moisture content and is often non-hazardous and can be disposed of in a suitable landfill site. It can sometimes be reused in the following applications:

*   as an alternative raw material in the cement industry;
*   as a treatment material for paint wastes, e.g. spray booth waste;
*   in waste stabilisation/solidification;
*   in the treatment of contaminated soils.

Cross-media effects
A side effect of this technique is the fact that the precipitate produced is fine and extremely slow to settle. This requires a settlement tank/clarifier that is designed for this purpose (often the settlement velocity is as slow as 0.18 m/h). Care should be taken with the addition of the Epofloc L1-R and flocculant so as to ensure that the flocculated particles settle in order to quickly leave behind fine particles of the calcium aluminium sulphate oxide.

The consumption of raw materials is as follows based on a flow rate of 5 m^3/h, 10 hours a day, five days a week, with an input sulphate level of between 2 500 mg/l and 8 000 mg/l, normally around 5 000 mg/l:

- aluminium hydroxychloride: 1 300 kg/week;
- liquid lime 18 wt-%: 4 000 kg/week;
- Epofloc L1-R: 5 kg/week;
- anionic flocculant: 3–5 kg/week.

The electrical consumption of the ultrasonic reactor is 120–140 watts.

The filter cake production is 5 000–6 000 kg/week.

Operational data
The plant is operated automatically. The required pH values are achieved using digital dosing pumps and pH controllers. The 4–20 mA signal from the pH controller is input into the dosing pump so the dosing is proportional. The ultrasonic reactor is started and stopped on the flow through the system. The ultrasonic reactor has its own control unit for setting the amplitude and power. One consideration from an operational/maintenance perspective is the cleanliness of the pH electrodes. Since the efficiency of the removal process is affected by pH, regular cleaning of the electrodes is required. In practice, this can be achieved with self-cleaning electrodes.

Applicability
The technique can be applied to new or existing plants. If the technique is retrofitted, this often will involve adding some dosing pumps and the ultrasonic reactor. Assuming the settlement tank or clarifier is of a suitably size, the technique can be applied to large or small plants. In the case of large plants, several ultrasonic reactors may be required to handle the flow (normally only required for flow rates of > 40 m^3/h).

Economics
The cost of the technique depends on the volume of waste water to be treated and on the pollutants to be removed. Costs of ultrasonic reactors are normally in the range of GBP 22 500–97 500 (EUR 28 700–124 000, average currency conversion rate for 2008: EUR/GBP = 0.7843).

Whilst the investment costs are quite high, this should be compared to the costs of tankering the waste off site, which would be around GBP 460–1 500 (EUR 590–1 900, average currency conversion rate for 2008: EUR/GBP = 0.7843) for a load of 20 tonnes, depending on the composition of the waste. This means that the payback time on the reactor is typically less than three months.

In addition to the payback time, there is an environmental benefit derived from the waste being treated at source.

Driving force for implementation
Whilst sulphate may not be seen as a pollutant with regard to the environment, it can generate problems with the sewer infrastructure, particularly the concrete sewers. This is a problem that is faced by industry discharging into water authority sewers throughout Europe.

Example plants
Rimex Metals Ltd, London, United Kingdom.

Reference literature
[158, Nash 2008]

5.1.2   Photocatalytic oxidation with titanium dioxide

Description
The technique is a low-temperature system based on photocatalysis that can degrade a range of organic compounds as well as destroy microorganisms in aqueous effluents. A variation of the technique can also be used to treat gas effluents (see Section 5.2.1).

The technique is simple to operate and with few moving parts. It is also highly reliable and robust. The system is capable of being scaled to a variety of throughput requirements, from litres to cubic metres per day, and can be operated either on a continuous flow or a batch basis, depending on the target material to be treated.

The basic configuration can use either a suspended photocatalyst that can be recovered for reapplication, or an immobilised photocatalyst coated on an inert substrate. The latter approach has, in general, a lower destruction efficiency than the former, but it reduces the need for a recovery plant, and is therefore simpler to build and to use.

With a suspended catalyst, a mixture of the target material to be treated, the catalyst and water is passed as a thin slurry film over a series of plates and exposed to UVA light. If sufficient degradation of the target material occurs, then the treated mixture can be passed through a catalyst recovery system, after which the water and treated target material can be released into the environment by discharge through a conventional water treatment system; the catalyst can be recycled for further use in the process. If further processing is required before transferring the degraded pollutant stream into the water treatment plant, a continuous loop system can be operated or, if batch processing is required, then the process mixture can be put into a holding tank for further treatment prior to discharge.

With an immobilised catalyst, the process is clearly simpler, whether a batch or a continuous flow is used.

Achieved environmental benefits
The photocatalytic process can be applied to industrial waste waters for:

* general organic pollutant destruction;
* specific pollutant degradation such as pharmaceutical- or pesticide-contaminated waters;
* toxicity reduction;
* biodegradability improvement;
* BOD/COD removal;
* odour and colour improvement.

Cross-media effects
Energy consumption (by the UV lamps as well as pumps to circulate the water effluents) is a cross-media effect associated with this technique.

No chemicals are consumed with the implementation of this technique.

The power consumption will be dependent on the reactor size and the energy requirement will depend on throughput. For a reactor suitable for treating ~ 2 200 l/d, or ~ 15 m^3/week, 200 lamps of 80 W each will be needed and with a treatment time of approximately 1.5 hours, the energy consumption will be about 24 kWh.

Operational data
The effectiveness of the technique will obviously depend on the technical set-up of the equipment and the substances being treated, and, as with all techniques, trials will be required prior to full-scale implementation. However, high destruction efficiencies (> 99 %) were reported for substances such as dyestuffs, nerve agents and pharmaceuticals.

This technique is probably only applicable to small-scale specialist treatment.

In 2009, there was no commercial application of this technique to the knowledge of the TWG for the review of this BREF.

Applicability
Advantages and disadvantages are given in Table 5.1.

Table 5.1: **Advantages and disadvantages associated with photocatalytic oxidation with titanium dioxide to treat waste waters**

	TiO$_2$ slurry	Immobilised TiO$_2$
Advantages	• Readily available • Relatively inexpensive • Highly photoactive • High surface area compared to immobilised TiO$_2$ (50 m^2/g) • No mass transfer effects	• No need to replace the catalyst after photocatalysis • Easy to replace • No coagulation • Proprietary method for achieving high surface area of TiO$_2$ coating
Disadvantages	• Need to remove slurry after photocatalysis • Can coagulate and lose activity	• Not readily available • Lower surface area than slurry • Problems of adherence and robustness

Economics
Indicative costs can only be given for a photocatalyst reactor system to treat micro-pollutants in waste water. Treatment of a particular micro-pollutant would have to be estimated on the basis of trial runs and pilot studies. Typically though, for a system that would treat about 2 200 l/d, or ~ 15 m^3/week, investment costs for an installed basic plant without ancillary equipment, such as analytical tools, would be in the range of GBP 400 000–500 000 (EUR 450 000–560 000, average currency conversion rate for 2009: EUR/GBP = 0.8982).

For the reactor mentioned above, the cost for treating about 140 litres will typically be GBP 1.20 (EUR 1.34, average currency conversion rate for 2009: EUR/GBP = 0.8982) and the weekly bill for 15 m^3 would be around GBP 132 (EUR 147, average currency conversion rate for 2009: EUR/GBP = 0.8982). Using this energy cost on a constant basis, an estimate of operating costs can be made by incorporating amortisation over five years, overhead labour costs, consumables (including replacement catalyst, or catalyst plates, and lamps), and servicing. Then, excluding plant overheads such as rent, rates, property maintenance, etc., annual operating costs are estimated to be about GBP 200 000 (EUR 220 000, average currency conversion rate for 2009: EUR/GBP = 0.8982).

Driving force for implementation
No information provided.

Example plants
No information provided.

Reference literature
[163, CEFIC 2009]

5.1.3 Combined electrochemical oxidation

Description

Electrochemical processes can be classified into two main groups:

- **direct electrolysis** (also called 'anodic oxidation', 'direct oxidation' or 'electrochemical incineration') by anodic oxidation in which the pollutant reacts at the anode surface with adsorbed hydroxyl radicals;
- **indirect electrolysis** where the pollutant reacts in the solution with an electrogenerated reagent produced at the anode (e.g. O_3, ClO^-, Cl_2, ClO_2) or at the cathode (e.g. H_2O_2).

Combined electrochemical oxidation processes combine electrochemical, photochemical and catalytic oxidation to achieve optimal results in the degradation of toxic and non-biodegradable organic substances.

The following combination can be used:

- anodic oxidation and cathodic generation of hydrogen peroxide (H_2O_2);
- cathodic generation of hydrogen peroxide and UV irradiation;
- catalytic electrochemical oxidation (*in situ* generation of hydrogen peroxide and specific catalysts);
- electrochemical generation of oxidising agents (e.g. H_2O_2, O_3), UV irradiation and varied catalysts.
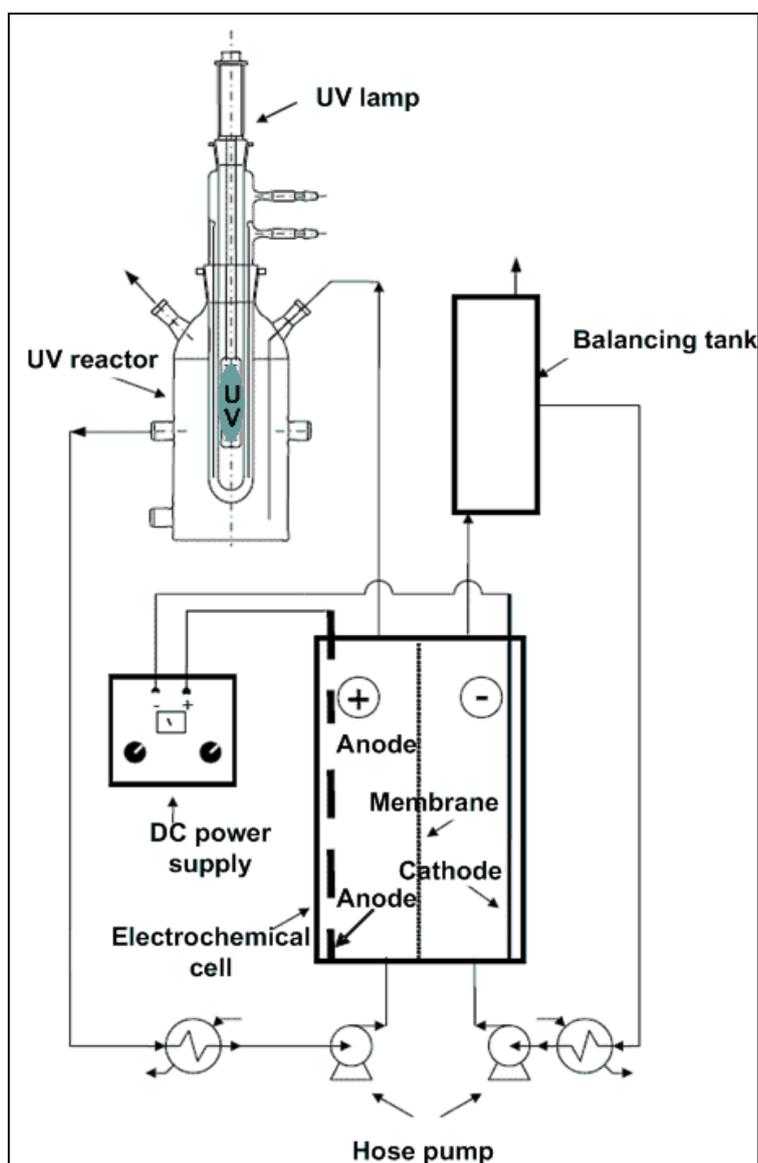
Figure 5.1:   Example of a combined electrochemical oxidation process

The objective of these combined electrochemical oxidation processes is the creation of hydroxyl radicals, the ultimate cause of oxidation of the organic matter present in the waste water.

Identification of the most suitable electrode materials generally necessitates carrying out specific tests adapted to the nature of the waste water that has to be treated.

Achieved environmental benefits
The technique allows toxic organic pollutants and non-biodegradable substances to be converted into more easily biodegradable organic compounds, or the total mineralisation of the organic pollutants (e.g. to convert them into water, salts and carbon dioxide).

The environmental performance of the technique is not only measured by the TOC, COD or specific compound reduction but also by taking into account the biodegradability improvement for further biological treatment.

A major advantage of electrochemical waste water treatment is the use of the waste water as an electrolyte.

Cross-media effects
Energy (to carry out electrolysis) is considered to be the most important cross-media effect.

Examples of consumables include:

- 9.2 kWh per m^3 for waste water with an incoming EDTA concentration of 500 ppm;
- reagents such as H_2O_2 are produced *in situ*.

Electrochemical methods are generally safe because of the mild conditions used (relatively low temperature and pressure) and the small amount and innocuous nature of the added chemicals.

Operational data
The nature of the electrode material strongly influences both the selectivity and the efficiency of the process [194, Martínez-Huitle and Ferro 2006].

Monitoring
A thorough monitoring of the following operating parameters is important:

- pH,
- temperature,
- TOC,
- concentration of the organic compounds in treated waste water,
- energy consumption.

Applicability
Advantages and disadvantages are given in Table 5.2.

Table 5.2:   Advantages and disadvantages associated with combined electrochemical oxidation

Advantages	Disadvantages
- Generally safe operation - Compared to techniques such as chemical oxidation, there is no transportation and storage of dangerous reactants (e.g. chlorine dioxide) - Relatively low consumption of energy (because of mild temperature and pressure to operate) - Can apply for treating waste waters with TOC < 5 000 ppm	- Low reaction rate in case of electrode fouling (by reaction products)

The technique is reported to be applicable to treat waste water loaded with persistent organic pollutants such as:

- pesticides and herbicides;
- polycyclic aromatic hydrocarbons (PAHs);
- volatile organic compounds (VOCs);
- chelating agents.

These contaminants can be found in waste waters from:

- pharmaceutical production;
- hospitals;
- the pulp and paper industry;
- the oil and petrochemical industry;
- municipalities.

Applications include:

- disinfection of drinking water;
- inactivation of bacteria and viruses;
- odour control;
- decolouration of dyestuffs;
- landfill leachates.

Economics
The lifetime of the electrodes may constitute one of the key economic parameters [194, Martínez-Huitle and Ferro 2006].

Economics associated with combined electrochemical oxidation are given in Table 5.3.

Table 5.3: Economics associated with combined electrochemical oxidation

Type of costs	Costs	Comments
Investment costs	EUR 100 000	For a waste water treatment capacity of 1 m^3/h
Operating costs	EUR 2.50 per m^3	To mineralise waste water with a concentration of 500 ppm EDTA
Source: [193, UBA AT 2009].		

Although investment costs for the equipment should be considered, the application for persistent waste water with a TOC value below 5 000 ppm is economically reasonable.

Driving force for implementation
New water legislation is the driving force for the implementation of this technique.

Example plants
- Lovö Waterworks, Stockholm, Sweden.
- VTU Technology, CoolOx water treatment plant, Graz, Austria.

Reference literature
[123, Tarr 2003] [193, UBA AT 2009] [194, Martínez-Huitle and Ferro 2006]

5.1.4 Supercritical water oxidation

Description
Supercritical water oxidation (SCWO) is a special application of the high-pressure variant of wet air oxidation (see Section 3.3.2.3.4.4.3). 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 5.2.

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.
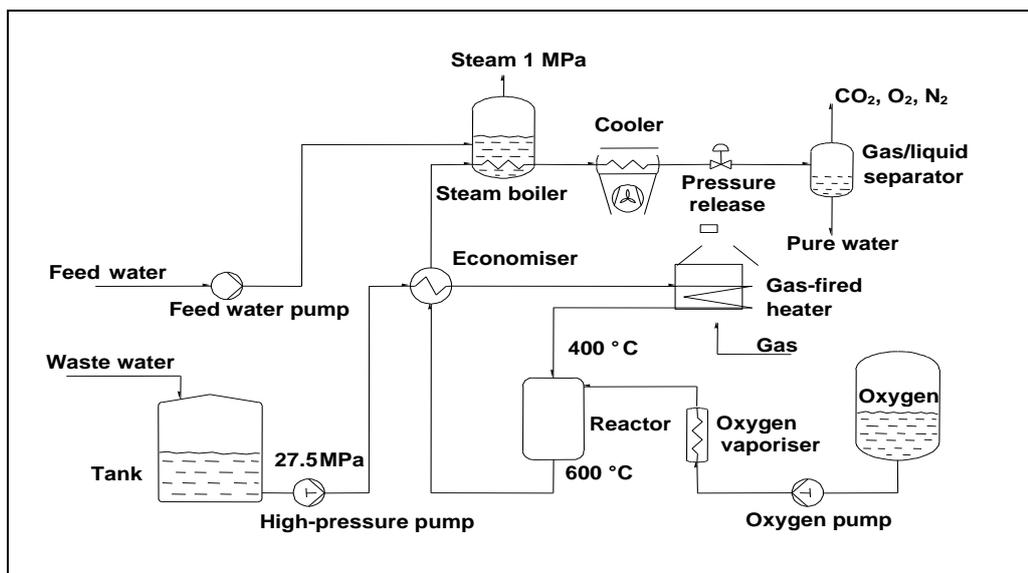
Figure 5.2:   Simplified flow sheet of the SCWO process

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.

Achieved environmental benefits
Abatement efficiencies associated with SCWO are given in Table 5.4.

Table 5.4:   Abatement efficiencies associated with SCWO

Pollutant	Abatement efficiency (%)	Comments
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
Dioxins	> 99.99 ([1])	574 °C, 3.7 min
([1]) [3, Environment Agency (England and Wales) 1997].		

Cross-media effects

Depending on the waste water influent, the gaseous effluent contains traces of nitrous oxide and acetic acid generated by the process, but also hydrogen halides as a degradation product of halogenated organic compounds, 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 enclosed.

Operational data

Monitoring

During the whole process, a thorough monitoring of operating parameters such as pressure, temperature and oxygen content should be carried out.

Applicability

SCWO is applied to contaminants with low biodegradability and/or high toxicity in the chemical, petrochemical and pharmaceutical industries. It also destroys dioxins and PCBs, while 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 and disadvantages are described in Table 5.5

Table 5.5:   Advantages and disadvantages associated with SCWO

Advantages	Disadvantages
• All organic content, irrespective of its properties, is destroyed • Very high destruction efficiency is achieved at relatively low temperatures, resulting in NO_X-free emissions • No dioxins are generated • Very short reaction time is necessary, resulting in short residence time and thus in low reactor volume • Can be combined with other downstream treatments	• Traces of nitrous oxide (N_2O) and acetic acid are likely to be found • Inorganic solids precipitate and might cause corrosion • Elevated chloride concentrations lead to increased corrosion thereby requiring specific types of steel

Economics
Operating costs are primarily determined by the energy costs associated with pumping the influent and compressing the air or oxygen. Costs between EUR 30/t and 100/t were reported [63, VITO 2010].

Driving force for implementation
Driving forces for implementation include relieving the subsequent biological treatment of COD/AOX loads that could have a disturbing, inhibiting or toxic effect.

Example plants
No information provided.

Reference literature
[3, Environment Agency (England and Wales) 1997] [63, VITO 2010]

5.1.5   Membrane distillation

Description
Membrane distillation (MD) is a thermally driven process in which only vapour molecules are transported through porous hydrophobic membranes. The liquid feed to be treated by MD must be in direct contact with one side of the membrane and does not penetrate the dry pores of the membranes. The hydrophobic nature of the membrane prevents liquid solutions from entering its pores due to the surface tension forces. As a result, liquid/vapour interfaces are formed at the entrances of the membrane pores. In MD, the membrane itself acts only as a barrier to hold the liquid/vapour interfaces at the entrance of the pores and it is not necessary to be selective as required in other membrane processes such as pervaporation. The main requirements for the MD process are that the membrane must not be wetted and only vapour and non-condensable gases must be present within its pores. The pore size of the membranes used in MD lies between 10 nm and 1 μm. The MD driving force is the transmembrane vapour pressure difference that may be maintained with one of the four following possibilities applied in the permeate side as shown in Figure 5.3.

1.   An aqueous solution colder than the feed solution is maintained in direct contact with the permeate side of the membrane giving rise to the configuration known as direct contact membrane distillation (DCMD). The transmembrane temperature difference induces a vapour pressure difference. Consequently, volatile molecules evaporate at the hot liquid/vapour interface, cross the membrane in the vapour phase and condense in the cold liquid/vapour interface inside the membrane module.
2.   A stagnant air gap is interposed between the membrane and a condensation surface. In this case, the evaporated volatile molecules cross both the membrane pores and the air gap to finally condense over a cold surface inside the membrane module. This MD configuration is called air gap membrane distillation (AGMD).
3.   A cold inert gas sweeps the permeate side of the membrane carrying the vapour molecules and condensation takes place outside the membrane module. This type of configuration is termed sweeping gas membrane distillation (SGMD).
4.   A vacuum is applied in the permeate side of the membrane module by means of a vacuum pump. The applied vacuum pressure is lower than the saturation pressure of the volatile molecules to be separated from the feed solution. In this case, condensation occurs outside the membrane module. This MD configuration is termed vacuum membrane distillation (VMD).
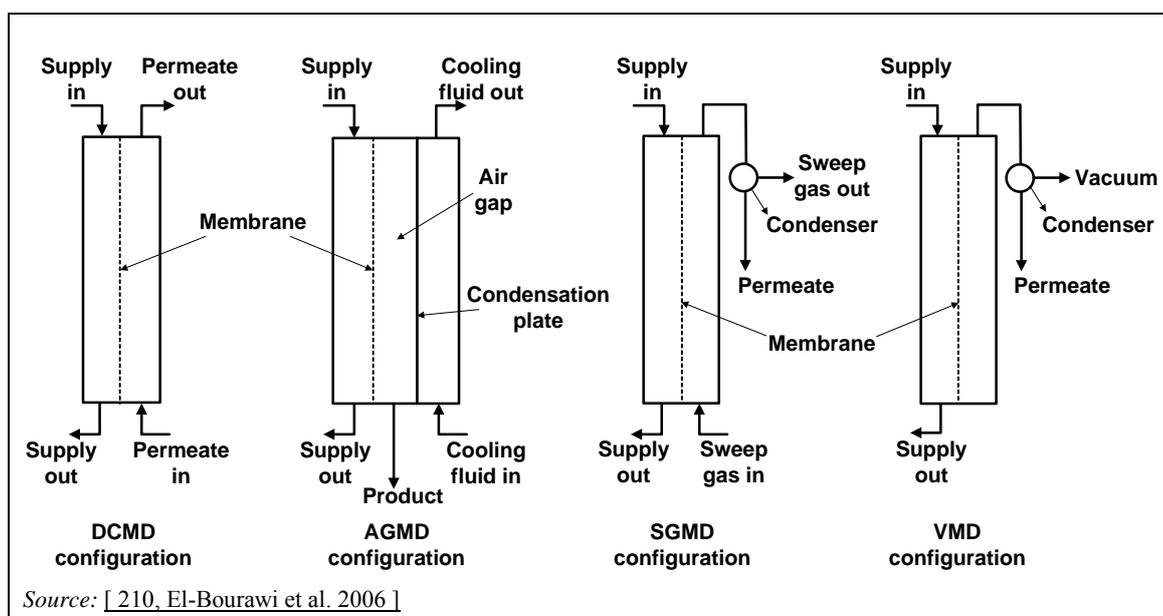
Figure 5.3:   Different types of MD configurations

The advantage of the MD process in comparison to the conventional separation processes is that it relies on a lower operating temperature and hydrostatic pressure. Feed solutions having temperatures much lower than their boiling point under pressures near atmospheric can be used. In contrast to pressure-based membrane processes, MD in principle does not require additives like acids or antiscalants because the membranes are a lot less sensitive to concentration polarisation or membrane pollution. Thus, MD does not require the supply mix to be subjected to a specific pretreatment.

Achieved environmental benefits
Separation/concentration of non-volatile compounds (e.g. ions, acids, colloids, macromolecules) from aqueous flows and the removal of trace amounts of VOCs like benzene, chloroform and trichloroethylene from water are the achieved environmental benefits of membrane distillation.

Cross-media effects
Cross-media effects include: relatively low permeate flux in comparison with pressure-based membrane processes such as RO, permeate flux decay due to concentration and temperature polarisation effects, membrane fouling and total or partial pore wetting, and high thermal energy consumption.

Operational data
In 2011, no industrial scale application of the MD process was reported.

Applicability
The MD process has been successfully applied on laboratory scale for the separation of non-volatile compounds from water like ions, colloids, macromolecules; for the removal of trace volatile organic compounds from water such as benzene, chloroform, trichloroethylene; and for the extraction of other organic compounds such as alcohols from dilute aqueous solutions. It has been applied for water desalination, environmental waste clean-up, water reuse and food processing. MD offers potential for water purification in the pharmaceutical, chemical and textile industries, for the concentration of fruit juices and milk processing, and in biomedical applications like the removal of water from blood. It could also be applied for separating azeotropic aqueous mixes (alcohol-water), for the concentration of cooling liquids (glycols), non-volatile acids and oil-in-water emulsions and in applications where high-temperature processing causes thermal degradation of the process flow. With the discharge of less harmful waste flows in mind, MD offers greater potential in the textile industry where waste water is contaminated with dyes.

Economics
Due to the use of very low pressures, which are associated with a low-cost installation (thinner piping, etc.) and fewer operational problems, investment and maintenance costs for MD are considerably lower than those of pressure-driven membrane processes like ultrafiltration (UF) and reverse osmosis (RO). If one assumes that MD technology is fully developed, the total production cost of a hypothetical DCMD desalination plant with 30 % internal heat recuperation for the production of clean water at $3\,800\,m^3/h$ can be estimated at EUR $0.55/m^3$, which is clearly lower than the cost of a RO installation with the same capacity (EUR $0.89/m^3$).

The expected cost for drinking water production in a large-scale MD desalination plant can currently be estimated at EUR $0.43–0.70/m^3$ (EUR $0.27–0.36/m^3$ when using residual heat). Further cost reductions are expected when the technique gets more mature. The cost efficiency of MD is to a great extent determined by the use of residual heat flows and/or alternative energy sources.

In contrast to conventional separation processes like distillation and RO, the MD process is carried out at a lower working temperature and pressure which results in lower energy costs. By using residual heat or alternative energy sources (solar, wind, etc.), the energy efficiency of a MD plant can be increased significantly.

Driving force for implementation
The driving force for implementation in comparison to the conventional separation processes is the requirement for a lower operating temperature and hydrostatic pressure.

Example plants
Despite the broad potential for application and the favourable cost estimate, MD is not yet generally accepted as a separation technique and is still not being implemented within industry on a large scale. The most recent developments tend to indicate an industrial breakthrough of MD for low-cost and sustainable desalting of sea water.

Reference literature
[63, VITO 2010] [210, El-Bourawi et al. 2006]

5.1.6   Naturally improved microorganisms to treat refractory TOC/COD

Description
The technique consists of the use of naturally improved microorganisms (e.g. prokaryotic cells or bacteria, photosynthetic bacteria or eukaryotes such as yeasts, fungi and photosynthetic microalgae) to treat waste waters loaded with refractory TOC/COD.

The technique consists of a three-step process:

- selection of naturally occurring microorganisms;
- generation of microbial variants with enhanced characteristics to treat the targeted pollutants in waste waters;
- introduction of the improved microorganisms into the water treatment process.

The technique is an alternative to other techniques such as chemical oxidation or incineration to treat waste waters which contain COD/TOC.

Achieved environmental benefits
A reduction of TOC/COD levels in water effluents is the environmental benefit of the technique.

Refractory TOC/COD abatement efficiencies associated with naturally improved microorganisms are given in Table 5.6.

Table 5.6: **Abatement efficiencies associated with naturally improved microorganisms to treat refractory TOC/COD**

Characteristics of the waste water treated	Abatement efficiency (% of TOC or COD removed)	Comments
100 g/l of TOC-containing acrylic acid polymers, metacrylic acid polymers and hydroquinone	70–97 TOC	Pilot scale
Effluent loaded with dimethylformamide	98 COD	Laboratory development
Effluent loaded with metformin	60 COD	2 days retention time for effluent which contains 95 % COD of metformin
Effluent loaded with methyl cyanide	98 TOC	—
Effluent loaded with sulphanilic acid and chloride from a pharmaceutical production plant	90 TOC	11 days retention time and chloride content of 32 g/l
Effluent loaded with aliphatic acids and phthalic acid derivatives	Up to 100 TOC	—
Source: [165, Fernández-Ulloa 2009].		

Cross-media effects
There are no significant cross-media effects associated with this technique.

Operational data
The generation of microbial variants is carried out in 'continuous' cultures, where the culture environment is constantly diluted, thus making it possible to maintain multiplying cell lines over long periods of time at a constant cell density. This is known as the 'turbidostat' principle.
Within a turbidostat, a constant elevated growth rate fosters the appearance of greater numbers of spontaneous mutations. The 'variants' produced tend to split more actively than other cells do, or to better utilise the resources available within the environment. Moreover, if they are maintained in suspension for as long as possible, their rate increases over time within the culture population, thus making them detectable and easier to isolate.

Applicability
The technique is generally applicable to new and existing installations in the industrial or municipal sectors.

Economics
Investment costs are made up of the treatment tank and the decanting system.

The technique can provide significant savings compared to incineration. At a plant producing acrylate resins in France, the total cost reduction is evaluated at 50 %.

The return on investment is expected to be < 2 years.

Driving force for implementation
The cost savings at installations with high incineration costs for treating waste water which contains refractory TOC/COD is the driving force for implementation.

Example plants
- TOTAL, France: effluent loaded with acrylic acid (industrial pilot phase).
- CIBA, Germany: effluent loaded with 4,4'-dinitrostilbene-2,2'-disulfonic acid (laboratory phase).
- Pharmazell, Germany: effluent loaded with sulphanilic acid (industrial pilot phase).
- Solvay, Belgium: effluent which contains phthalic acid (industrial pilot phase).

Reference literature
[165, Fernández-Ulloa 2009]

5.2 Waste gas treatment techniques

5.2.1 Photocatalytic oxidation with titanium dioxide to treat VOCs

Description
Photocatalytic oxidation, also called photocatalysis, is a technique used to degrade many pollutants (e.g. VOCs, sulphur compounds, nitrogen compounds, odours, and bacteria) contained in waste gases by oxidation. A variation of the technique can also be used to treat water effluents (see Section 5.1.2) in low concentrations.

This technique is based on a two-step reaction process that requires a catalyst (TiO_2 is commonly used) and an irradiation system to activate the catalyst (ultraviolet rays from artificial lamps or sunlight can be used).

The combined action of UV rays and TiO_2 turn a portion of available water vapour in the air into two highly reactive, strong oxidisers: hydroxyl radicals (OH) and superoxide ions (O_2^-). These OH radical elements have twice as much oxidation power as chlorine and decompose organic matter (e.g. VOCs, odours) and bacteria into carbon dioxide (CO_2).

Achieved environmental benefits
Removal of VOCs, sulphur compounds, nitrogen compounds (e.g. NO_X), and odorous substances from waste gases is the main achieved environmental benefit of the technique.

As an example of the environmental benefits that can be achieved, Table 5.7 shows the results of a measurement campaign carried out by a company in France that has implemented the technique to abate odours from a building storing sludge.

Table 5.7: Abatement efficiencies associated with photocatalytic oxidation with titanium dioxide to treat waste gas

Pollutants abated	Abatement efficiency (%) [1]	Comments
Sulphur compounds (dimethyl sulphide, dimethyl disulphide)	98	No complaint from neighbours after implementation of the technique. A 'nose jury' determined that there were no odours within a 50 m radius of the building
Ketones (2-butanone, acetone)	70–95	—
Aromatics (ethylbenzene)	95	—
[1] This building has a ground surface of 1 500 m^2 and a height of 10 m. The walls are equipped with photocatalytic media (300 m^2). The air crosses the walls of the building with ventilators whose flow is 40 000 m^3/h. The investment costs of the building were EUR 334 400.		
NB: NI = no information provided.		
Source: [155, Paillier 2008].		

In contrast to techniques that are exclusively based on adsorption and that result in pollutant transfer with the need for supplementary treatments, photocatalysis completely mineralises the organic pollutants.

Cross-media effects
The following cross-media effects are associated with low-temperature NO_X oxidation:

- energy consumption (by the UV lamps as well as fans for circulating the air effluents);
- CO_2 emissions;
- replacement of the catalyst (lifetime of about three years). [227, CWW TWG 2009]

No chemicals are consumed in this technique.

Operational data
The technique is mostly efficient for treating effluents with a low concentration of pollutants (i.e. between $0 \, g/m^3$ and $30 \, g/m^3$; with optimal efficiency for concentrations of around $1 \, g/m^3$) and a low flow rate (optimal efficiency for flows of between $10 \, m^3/h$ and $1\,500 \, m^3/h$) [122, INERIS 2009].

The technique is mainly advantageous for directly treating emissions from surface sources because there is no influence of the temperature in the range of 20–80 °C [122, INERIS 2009].

Humidity affects the efficiency of the technique. A relative humidity rate of 40 % is considered ideal [122, INERIS 2009].

Applicability
The technique can be used in purifying/deodorising gaseous effluents which contain only traces of pollutants [123, Tarr 2003]. It is used to treat air effluents from buildings where liquid effluents or sludge are stored (see example above) [122, INERIS 2009].

Concerning odours, the technique is particularly useful for compounds with an olfactory threshold in the order of 1 ppbv or less, and if the concentration is low enough [123, Tarr 2003].

Economics
Operating costs arise mainly from the UV lamps and the corresponding electrical consumption.

Driving force for implementation
The driving force for implementation of this technique is to limit odorous nuisances around installations (e.g. from sludge).

Example plants
Ahlstrom paper production plant, Pont L'Evêque, France.

Reference literature
[122, INERIS 2009] [123, Tarr 2003] [155, Paillier 2008]

5.2.2 Multiple pollutant removal technique using ceramic filters and catalytic reduction

Description
The core of the technique consists of treating waste gases at up to 400 °C by passing them through ceramic filter elements (called candles) incorporating a catalyst (see Figure 5.4). Pollutants contained in the waste gases such as dust, acids, NO_X, heavy metals and PCDDs/PCDFs are abated in a single, all-in-one, treatment unit where the following takes place:

- Acid pollutants (e.g. HCl, SO_2, HF) are neutralised (by injection, e.g. of sodium bicarbonate, lime) upstream of the ceramic and catalytic filter.
- NO_X is reduced to N_2 and H_2O by passing through the ceramic and catalytic filter (urea or ammonia is injected into the waste gases upstream of the filter).
- Dust is abated by filtration using ceramic candles. An air pulse system is used to clean the candle elements online. The dusty materials are recovered in a storage silo.
- PCDDs/PCDFs are abated by the catalytic system or adsorbed on a filter.
- Heavy metals are adsorbed onto the adsorbing filter.
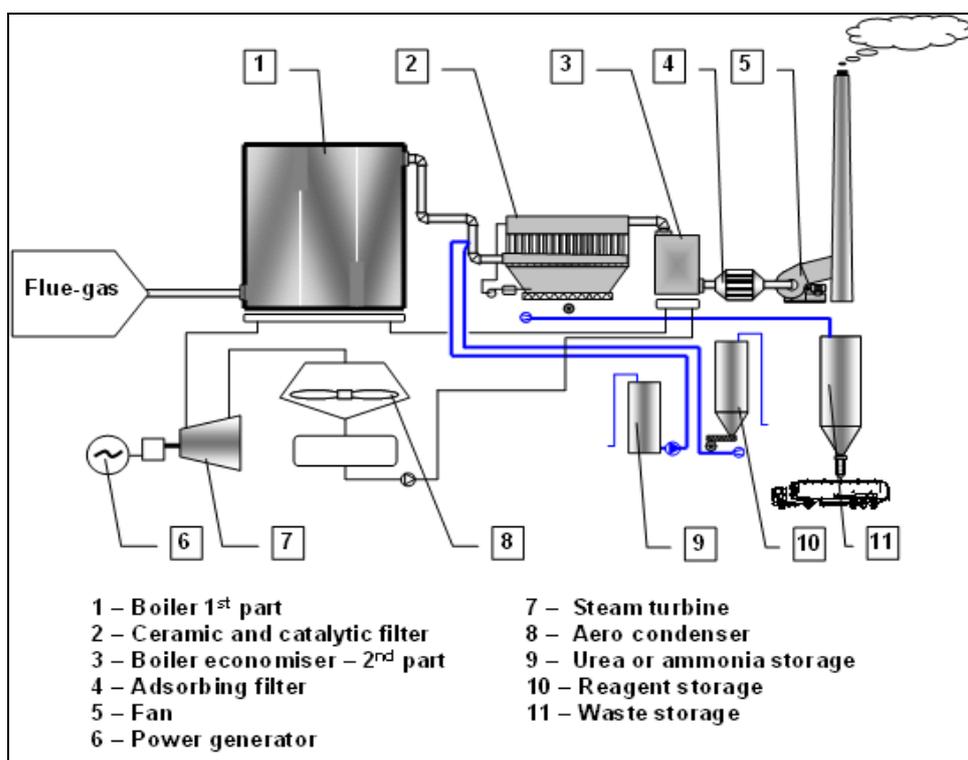
Figure 5.4: Layout of the multiple pollutant removal technique using ceramic filters and catalytic reduction

For each application of the technique, a specific study is performed to determine which kind of reagent should be used, depending on the waste gas temperature, the pollutants' composition and the treatment requirements.

This technique is an alternative to the conventional combinations of an ESP (see Section 3.5.1.4.4) and SCR (see Section 3.5.1.5.3) or bag filters (see Section 3.5.1.4.7) and SCR (see Section 3.5.1.5.3).

Achieved environmental benefits
A reduction of the following emissions to air can be expected with this technique: HCl, SO_2, HF, NO_X, dust, PCDDs/PCDFs and heavy metals.

Abatement efficiencies and emission levels associated with the multiple pollutant removal technique are given in Table 5.8.

Table 5.8: Abatement efficiencies and emission levels associated with the multiple pollutant removal technique

Pollutants abated	Emission level (mg/Nm^3)	Abatement efficiency (%)
NO_X	< 80 ([1])	98
Dust	< 5 ([1])	99.9
SO_X	< 50 ([1])	97
HCl	< 10 ([1])	97
HF	< 5 ([1])	97
PCDDs/PCDFs	< 0.000 1 ([1])	NI
([1]) 8 % O_2 dry.		
NB: NI = no information provided.		
Source: [153, Maguin 2008].		

Cross-media effects

The following cross-media effects are associated with this technique:

- the generation of waste (i.e. candles cannot be recycled);
- energy consumption;
- consumption of reagents;
- noise emissions from fans, reagent pumps and compressors, which have to be equipped with adequate noise containment techniques.

Specific safety measures may need to be used depending on the reaction of ammonia or urea with substances in the waste gas.

Consumables associated with the multiple pollutant removal technique are given in Table 5.9.

Table 5.9: Consumables associated with the multiple pollutant removal technique

Parameter	Consumption	Comments
Compressed air (for 1 000 Am^3/h of waste gas volume treated)	0.003 Nm^3/h	—
Energy (kWh for 1 000 Am^3/h of waste gas volume treated)	1.25 kWh	—
Reagent for acid gases' neutralisation	Depends on acid gas load and temperature and reagent used	Lime or sodium bicarbonate
Reagent for NO_X removal	Close to stoichiometry	Urea or NH_3
Reagent for heavy metals (HM) removal	Depends on HM load and temperature and reagent used	Activated carbon or equivalent
NB: NI = no information provided. *Source:* [153, Maguin 2008].		

Operational data

To ensure reliable operation, the pressure drop across the ceramic filter should be monitored continuously. Also, the pressure drop in the furnace needs to be regularly monitored to run the process fan. Reagent consumption is automatically adjusted based on the pollutants monitored.

Applicability

The technique is an alternative to the combination of an ESP and SCR or bag filters and SCR in production processes where several pollutants are present in the waste gases.

Application limits and restrictions are given in Table 5.10.

Table 5.10: Application limits and restrictions associated with the multiple pollutant removal technique

Issue	Limits/restriction
Pressure drop (no duct taken into account)	2–2.5 kPa
Ceramic and catalytic candles	6–8 years (expected)
Temperature loss between inlet/outlet of filter	20–30 °C
Source: [153, Maguin 2008].	

Advantages and disadvantages are given in Table 5.11.

Table 5.11: Advantages and disadvantages associated with the multiple pollutant removal technique

Advantages	Disadvantages
•Compact design: The unit is two to three times more compact than other process installations (ESP + SCR or bag filter + SCR) •High filtration efficiency: Dust emissions are typically < 5mg/Nm^3 regardless of inlet dust concentration •Reagent consumption optimisation: a reaction through a dust cake and an efficient reagent chemical reactivity at a high temperature •Improved selenium treatment: Tests show that the system permits selenium emission level standards to be reached more easily •Reduced filtration residues: Reagent consumption optimisation leads to lower production of filtration residues and, therefore, to a reduced volume to treat (recycling or disposal) •NO$_X$ reduction optimisation: The integration of the catalyst system allows flexibility of the NO$_X$ reduction due to its large treatment surface •Reduced maintenance: The equipment is reduced due to the degree of the integration of the technique system, thereby minimising maintenance costs •Furnace/boiler yields improved by 10 %: For units equipped with an energy recovery system, the process permits, on the one hand, an increase in the availability of the heat exchanger located beyond the filter by limiting fouling and, on the other hand, increased energy efficiency by reducing the fume temperature allowed after the heat exchanger •Lower operating costs: Low costs are a consequence of the above factors. Depending on the characteristics of the installation, savings can reach up to 30 % compared to conventional systems	•Emerging technique: The first unit was set up in the east of France in January 2004, and was installed in a slaughterhouse waste energy recovery unit •Lifetime of ceramic and catalytic candles •Cost of ceramic and catalytic candles •Use of reagents and formation of solid or liquid waste

Economics

The costs of the technique vary widely, mainly depending on the pollutants to be abated and the waste gas volume to be treated. Cost information is given in Table 5.12.

Table 5.12: Economics associated with the multiple pollutant removal technique

Investment costs (k EUR/ 1 000 Nm^3/h)	Annual operating costs
50–80	Depends on the quantity of pollutants that need to be removed
Source: [153, Maguin 2008].	

Driving force for implementation
The driving forces for implementation include:

- a reduction in costs of abatement;
- compliance with environmental legislation.

Example plants
No information provided.

Reference literature
[153, Maguin 2008]

6   CONCLUDING REMARKS AND RECOMMENDATIONS FOR FUTURE WORK

Timing of the review process
The key milestones of the review process are summarised in Table 6.1.

Table 6.1:   Key milestones of the review process of the BREF for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector

Key milestone	Date
Reactivation of the TWG	28 November 2007
Call for wishes	24 January 2008
Kick-off meeting	16 to 18 June 2008
Collection of bulk of information, including first survey with installation-specific questionnaires	July 2008 to February 2009
First draft of the revised CWW BREF	29 September 2009
End of commenting period on first draft (1 055 comments received)	27 November 2009
First meeting of the subgroup on the analysis of questionnaires	11 to 12 January 2010
Second meeting of the subgroup on the analysis of questionnaires	24 to 25 June 2010
Second draft of the revised CWW BREF	15 July 2011
End of commenting period on second draft (998 comments received)	15 October 2011
Third meeting of the subgroup on the analysis of questionnaires	11 to 13 April 2012
Second survey with installation-specific questionnaires	October 2012 to January 2013
Final TWG meeting	10 to 13 December 2013

During the review process, a total of eleven site visits in four countries were carried out.

Sources of information and information gaps
During the review process, several hundred documents were shared by the TWG via the Commission's BAT information system (BATIS). These included approximately 110 questionnaires with specific data on waste water treatment plants. Major contributors of information were CEFIC (European Chemical Industry Council) and several EU Member States (Austria, Belgium, Czech Republic, Denmark, France, Germany, Ireland, Italy, the Netherlands, Poland, Portugal, Spain, Sweden, and the United Kingdom). Other contributors to the review process were Finland, CONCAWE (European Oil Company Organisation for Environment, Health and Safety), EEB (European Environmental Bureau), HWE (Hazardous Waste Europe), and the US EPA (United States Environmental Protection Agency). All these documents were assessed by the EIPPCB together with additional documents that could not be shared via BATIS due to various reasons (e.g. confidentiality, copyright restrictions). As a result, approximately 250 documents are referenced in the revised BREF (REFERENCES).

Degree of consensus reached during the information exchange
At the final TWG meeting in December 2013, a high degree of consensus was reached on the BAT conclusions. However, five dissenting views were expressed. Two of these dissenting views became obsolete after the forum for the exchange of information pursuant to Article 13 of the Directive had given a consensual opinion on those issues. The three remaining dissenting views are given in Table 6.2.

Table 6.2:   Split views

BAT conclusion	View expressed by	Split view
Table 4.1	United Kingdom	The United Kingdom expressed a dissenting view that the footnote on the BAT-AEL for emissions of TSS to water concerning the production of soda ash and titanium dioxide should be formulated in a more generic way, namely: 'This BAT-AEL may not apply to inorganic effluents in the case of high TSS loads and slow settlement rates'.
Table 4.2	Austria	Austria expressed a dissenting view that the BAT-AEL for emissions of total nitrogen (TN) to water may not apply when the main pollutant load originates from biological processes (e.g. fermentation processes for the production of active pharmaceutical ingredients).
Section 4.5.2	Austria, Denmark, Germany, the Netherlands	Austria, Denmark, Germany and the Netherlands expressed a dissenting view that BAT-AELs for emissions to air should be included in the BAT conclusions.

Consultation of the Forum and subsequent formal adoption procedure of the BAT Conclusions

In accordance with Article 13(3) of the Directive, the Forum gave its opinion on the draft Best Available Techniques (BAT) reference document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector at its meeting of 24 September 2014:

1. The Forum welcomed the draft Best Available Techniques (BAT) reference document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector as presented by the Commission.
2. The Forum acknowledged the discussions held at its meeting of 24 September 2014 and agreed that the changes to the draft Best Available Techniques (BAT) reference document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector, as proposed in Annex A, should be included in the final document.
3. The Forum reaffirmed the comments in Annex B as representing the views of certain members of the Forum but on which no consensus existed within the Forum to include them in the final document.

Subsequently, the Commission took the opinion of the IED Article 13 Forum into account when preparing the draft Commission Implementing Decision establishing best available techniques (BAT) conclusions for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector. The IED Article 75 Committee, at its meeting of 30 June 2015, gave a positive opinion on this draft Commission Implementing Decision.

Subsequently, the Commission Implementing Decision (EU) 2016/902 establishing best available techniques (BAT) conclusions for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector was adopted on 30 May 2016 and published in the Official Journal of the European Union (OJ L 152, 9.6.2016, p. 23).

Recommendations for future work

The information exchange revealed a number of issues that should be addressed during the next reviews of the chemical BREFs. These issues include:

- consideration of techniques to reduce water usage during the next reviews of the other chemical BREFs (i.e. CAK, LVOC, LVIS-AAF, LVIC-S, OFC, POL, SIC);
- further collection of performance data on waste water pretreatment techniques in order to assess the possibility of setting BAT-associated environmental performance levels (BAT-AEPLs) during the next reviews of all chemical BREFs;

- further collection of short-term emission data in order to assess the possibility of setting short-term BAT-AELs for emissions to water during the next review of the CWW BREF;
- further collection of information on water saving measures, in particular through questionnaires, and further exploration of the 'net pollution' issue during the next review of the CWW BREF;
- further collection of information on the low-loaded biological treatment step during the next review of the CWW BREF;
- further collection of information on the treatment of waste water with high TOC/COD concentrations and high proportions of refractory organic compounds during the next review of the OFC BREF;
- further collection of emission data for ammoniacal nitrogen from sites without biological treatment in order to assess the possibility of setting BAT-AELs for emissions to water during the next review of the CWW BREF;
- further collection of information on economics and cross-media effects of the techniques that can be used to abate total phosphorus during the next review of the CWW BREF;
- further collection of information on the treatment of waste water from the production of iodinated X-ray contrast agents during the next review of the OFC BREF;
- further collection of information on the treatment of waste water from the production of propylene oxide and epichlorohydrin via the chlorohydrin process during the next review of the LVOC BREF;
- further collection of information on emissions of cadmium, lead and mercury during the next reviews of all chemical BREFs;
- further collection of installation-specific data with relevant contextual information on emissions to air in order to assess the possibility of setting BAT-AELs for emissions to air during the next reviews of all chemical BREFs;
- collection of information on the energy efficiency of waste water treatment plants during the next review of the CWW BREF.

Suggested topics for future R&D work

The Commission is launching and supporting, through its Research and Technological Development 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 European IPPC Bureau of any research results that are relevant to the scope of this document (see also the fifth section of the Preface of this document).

7 ANNEXES

7.1 Annex I. Joint operation of industrial and municipal WWTPs

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 for 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 requirements of the agreement:

- pH of the effluent ranging between 5.5 and 8.5 (potentially 9.5);
- temperature of the effluent < 30 °C;
- effluent should not contain 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, TP, 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 properly handle flow variations, start-up/shutdown 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 and 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 a municipal sewerage system and an industrial site);
- the obligations of the local authority include:
  - 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 issues.

Example of cooperation between a municipal and an industrial WWTP with a positive synergistic effect (Germany)

In Section 1.6.3.2, it was mentioned that there are normally no advantages or disadvantages to 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 microorganisms 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 investment costs and the mutual discharge reduces the nitrogen load (sum of ammonium, nitrite and nitrate) into the receiving river by 1 000 kg per day, compared to the separated discharges before.
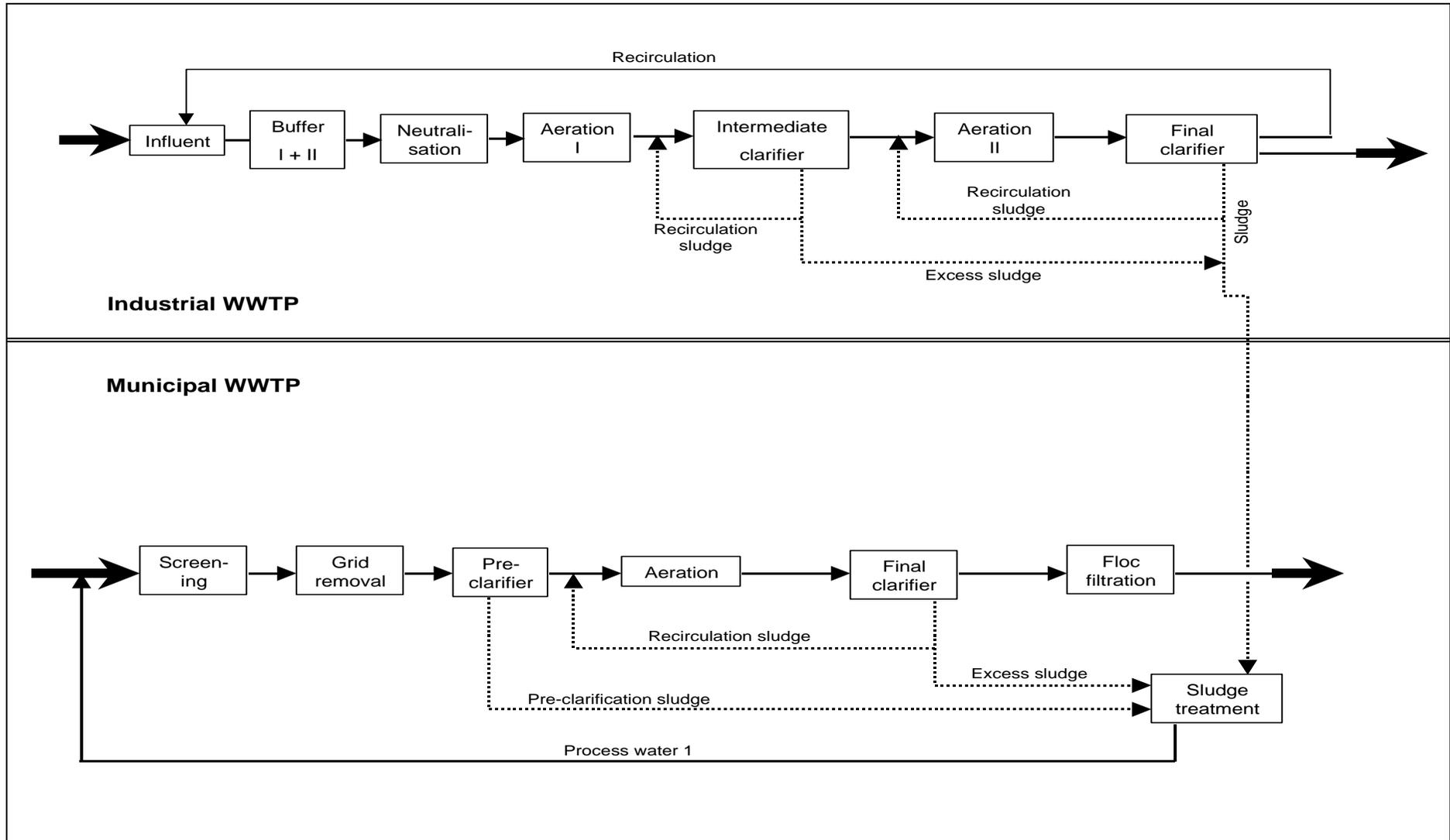
Figure 7.1: Cooperation between an industrial WWTP and a municipal WWTP: previous situation
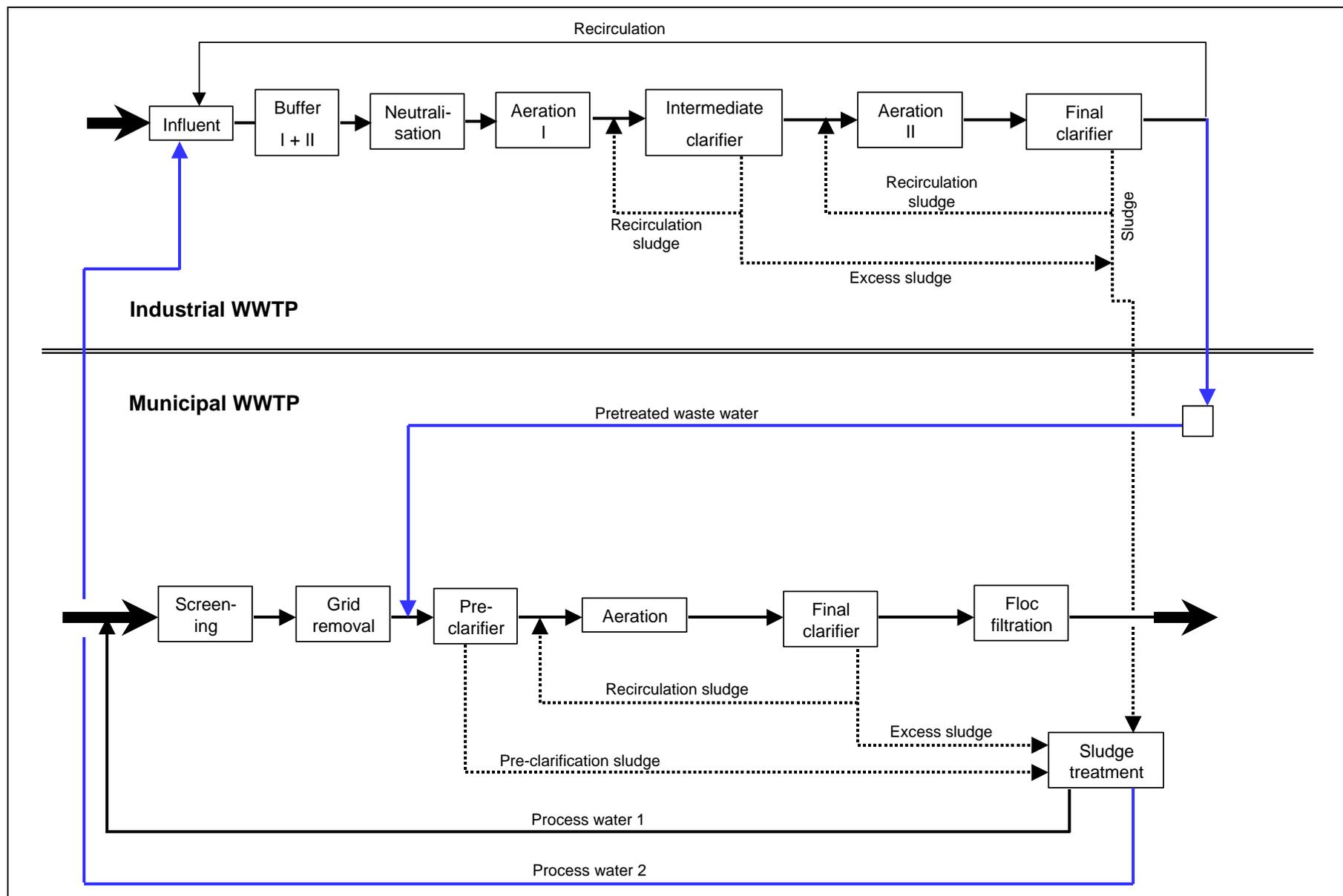
Figure 7.2: **Cooperation between an industrial WWTP and a municipal WWTP: current situation**

7.2 Annex II. General information on the characteristics of the WWTPs for which data were reported for the first review of the CWW BREF

Table 7.1: Characteristics of the WWTPs for which data were reported for the first review of the CWW BREF

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used ([1])	Unit operations ([1])	Average waste water treated (10^3 m^3/yr)	Year
#01	DE	OFC	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Chemical phosphorus precipitation - Sand filtration for final solids removal	1) Equalisation and neutralisation 2) Aeration 1 3) Sedimentation 1 4a) Combined aeration and sedimentation 2a 4b) Combined aeration and sedimentation 2b 5) Aeration 3 6) Sedimentation 3 7) Sand filtration	1 400	2007
#02	DE	CAK, LVIC-AAF, LVIC-S, SIC, LVOC, OFC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Chemical phosphorus precipitation - Sedimentation for final solids removal	1) Neutralisation 2) Screening 3) Primary sedimentation 4) Aeration basins 5) Secondary sedimentation 6) Sludge thickening and dewatering	122 000	2007
#03	DE	CAK, LVOC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Chemical phosphorus precipitation - Sedimentation for final solids removal	1) Primary sedimentation 2) Aeration (incl. nitrification/denitrification) 3) Secondary sedimentation 4) Sludge treatment	10 000	2011
#041	DE	SIC, OFC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sedimentation for final solids removal	1) Screening, grit chamber 2) Neutralisation 3) Equalisation 4) Two-stage biological treatment (waste water of production plants is routed to stage 1 (activated sludge treatment); municipal waste water is routed to stage 2 (activated sludge treatment) in addition to effluent of stage 1)	7 800	2007
#042	DE	SIC, OFC, POL	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Screening, grit chamber 2) Precipitation/flocculation 3) Sedimentation 4) Neutralisation	4 100	2007

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used (^{1})	Unit operations (^{1})	Average waste water treated (10^3 m^3/yr)	Year
#05	DE	SIC	Direct, to a river	- Physico-chemical treatment only - Filtration for final solids removal	- Waste water containing chromium and ammonium: 1) Stripping 2) Chemical reduction of chromate 3) Precipitation of metals 4) Filtration - Waste water containing nitrate: 1) Precipitation, filtration and ion exchange to remove metals 2) Reverse osmosis, evaporation, and crystallisation to recover nitrate	9.3	2007
#06	DE	OFC	Direct, to a river	- Waste water incineration - Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Chemical phosphorus precipitation - Sedimentation for final solids removal	- Highly concentrated waste water streams (10 % of the volume, 50 % of the TOC load): 1) Concentration, if necessary 2) Incineration - Bulk of waste water streams: 1) Neutralisation 2) Primary sedimentation 3) Two-stage biological treatment, together with municipal waste water 4) Secondary sedimentation	4 000	2007
#07	DE	OFC	Direct, to a river	- Biological treatment using activated sludge (tower biology) - Nitrification/denitrification - Sedimentation for final solids removal	1) Neutralisation 2) Primary sedimentation 3) First stage biological treatment: trickling filters 4) Second stage biological treatment: activated sludge plant, three trains parallel 5) Secondary sedimentation	3 000	2007
#08	DE	OFC	Direct, to a river	- Biological treatment using a membrane bioreactor - Nitrification/denitrification - Chemical phosphorus precipitation - Ultrafiltration for final solids removal	1) Equalisation 2) Stage 1: activated sludge treatment of highly polluted waste water 3) Stage 2: activated sludge treatment of moderately polluted waste water plus effluent of stage 1; stage 2 consists of 6 aeration tanks operated as a biological cascade; the last tank is designed as a membrane bioreactor	500	2007

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used ([1])	Unit operations ([1])	Average waste water treated (10^3 m^3/yr)	Year
#09	DE	OFC	Indirect, to a municipal WWTP	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sedimentation for final solids removal	1) Equalisation, neutralisation 2) Denitrification 3) Two-stage biological treatment, first stage with pure oxygen, second stage: nitrification 4) Secondary sedimentation	1 300	2007
#10	DE	LVIC-AAF, LVIC-S, LVOC, OFC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Chemical phosphorus precipitation - Flotation for final solids removal	1) Neutralisation, preliminary sedimentation 2) Denitrification 3) Two-stage biological treatment 4) Secondary sedimentation 5) Flotation	24 000	2007
#11	DE	SIC, LVOC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Chemical phosphorus precipitation - Flotation for final solids removal	1) Equalisation, neutralisation, primary sedimentation 2) Denitrification 3) First stage of biological treatment 4) Second stage of biological treatment, incl. nitrification 5) Secondary sedimentation 6) Flotation	13 000	2007
#12	DE	OFC	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Chemical phosphorus precipitation - Sedimentation for final solids removal	1) Neutralisation, primary sedimentation 2) Biological treatment with denitrification 3) Secondary sedimentation	1 800	2011
#13	DE	OFC	Direct, to a river	- Biological treatment using activated sludge (tower biology) - Chemical phosphorus precipitation - Sedimentation for final solids removal	1) Neutralisation, primary sedimentation 2) Biological treatment in tower biology, additionally charcoal 3) Secondary sedimentation, integrated	2 700	2011
#14	DE	CAK, LVIC-AAF, OFC	Direct, to a river	- Biological treatment using activated sludge (flat tank and tower biology) - Nitrification/denitrification - Chemical phosphorus precipitation - Sedimentation for final solids removal	1) Neutralisation, flocculation, primary sedimentation 2) Two-stage biological treatment in basins and in tower biology 3) Secondary sedimentation	16 000	2011
#15	DE	OFC, POL	Direct, to a river	- Biological treatment using activated sludge (tower biology) - Sedimentation for final solids removal	1) Neutralisation, primary sedimentation 2) Biological treatment in tower biology 3) Secondary sedimentation, integrated	2 000	2011

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used (^{1})	Unit operations (^{1})	Average waste water treated (10^3 m^3/yr)	Year
#16	DE	OFC, POL	Direct, to a river	- Biological treatment using activated sludge (tower biology) - Nitrification/denitrification - Sedimentation for final solids removal	1) Neutralisation primary sedimentation, equalisation 2) Four-stage biological treatment: denitrification, anaerobic reactors, activated sludge process in aeration tower biology and in aeration basins 3) Secondary sedimentation	4 600	2011
#17	FR	CAK, LVOC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Primary sedimentation 2) Neutralisation 3) Aeration 4) Secondary sedimentation	1 300	2007
#18	IT	LVOC, OFC	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Pretreatment with Fenton reaction for influents containing peroxides and surfactants 2) Neutralisation 3) Activated sludge process 4) Secondary sedimentation 5) Sludge thickening	1 800	2007
#19	NL	OFC	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Equalisation/neutralisation 2) Aeration 3) Secondary sedimentation 4) Biofiltration to remove odour from waste gases 5) Sludge thickening	630	2007
#21	DE	CAK, LVIC-S, SIC, LVOC, OFC, POL	Direct, to a river	- Biological treatment using activated sludge (tower biology) - Nitrification/denitrification - Flotation for final solids removal	1) Neutralisation 1 2) Primary sedimentation 3) Buffer tank, Optional: Aeration, Nitrification 4) Neutralisation 2 5) Denitrification 6) Aeration, Nitrification 7) Sedimentation 8) Flotation 9) Sludge thickening, conditioning, dewatering, and digestion	2 300	2007
#22	DE	CAK, LVIC-AAF, LVIC-S, SIC, LVOC, OFC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sedimentation for final solids removal	1) Primary sedimentation 2) Neutralisation 3) Biological treatment using activated sludge 4) Secondary sedimentation 5) Polishing pond	15 000	2007

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used (^{1})	Unit operations (^{1})	Average waste water treated (10^3 m^3/yr)	Year
#24	UK	LVOC, OFC, POL	Indirect, to a municipal WWTP	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Oil-water separation 2) Primary sedimentation 3) Equalisation 4) Neutralisation 5) Air Flotation 6) Aerobic biodegradation using a biofilter 7) Aerobic biodegradation using activated sludge 8) Secondary sedimentation	270	2007
#25	UK	OFC	Direct, to an estuary	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Equalisation 2) Neutralisation 3) Primary sedimentation 4) Aeration 5) Secondary sedimentation 6) Sludge thickening	730	2007
#26	UK	LVOC	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Oil-water separator (API) 2) Parallel plate interceptors 3) Primary sedimentation 4) Air flotation 5) Aerator 6) Lagoon	1 100	2007
#27	UK	CAK, LVIC-AAF, LVOC	Direct, to a canal	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Stripping 2) Neutralisation 3) Flocculation and precipitation 4) Sedimentation 5) Sludge dewatering	1 000	2007
#28	UK	OFC	Direct, to an estuary	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Equalisation 2) Neutralisation 3) Flocculation 4) Primary sedimentation 5) Aeration 6) Secondary sedimentation 7) Sludge dewatering 8) Waste gas biofilter 9) Waste gas carbon adsorber	730	2007

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used ([1])	Unit operations ([1])	Average waste water treated (10^3 m³/yr)	Year
#29	UK	OFC, POL	Direct, to the sea	- Biological treatment using a fixed-bed process - Flotation for final solids removal	1) Equalisation and neutralisation 2) Anaerobic digestion 3) Biological aerated filters 4) Air flotation 5) Sludge dewatering	310	2005
#31	UK	LVIC-S	Indirect, to a lagoon	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Filtration 2) Sedimentation	370	2007
#32	UK	SIC	Direct, to a river	- Physico-chemical treatment only - Sand filtration for final solids removal	1) Precipitation of lead 2) Sedimentation 3) Flocculation of overflow 4) Air flotation 5) Sand filtration	15	2007
#33	UK	OFC	Direct, to the sea	- Biological treatment using an expanded-bed process - Chemical phosphorus precipitation - Flotation for final solids removal	1) Equalisation 2) Neutralisation 3) Biological treatment using moving-bed bioreactors 4) Chemical precipitation 5) Air flotation 6) Sludge thickening (centrifugation)	270	2007
#34	SE	OFC	Direct, to the sea	- Biological treatment using an expanded-bed process - Nitrification/denitrification - Chemical phosphorus precipitation - Sand filtration for final solids removal	1) Screening 2) Heating 3) Biological treatment with biofilm process using plastic carriers 4) Flotation 5) Activated carbon 6) Precipitation 7) Sand filtration 8) Sludge thickening (centrifugation)	400	2007
#35	FR	LVIC-AAF, LVOC, POL	Direct, to a river	- Physico-chemical treatment only - Flotation for final solids removal	1) Screening 2) Neutralisation 3) Oil-water separation 4) Sand/grit removal 5) Coagulation/flocculation 6) Flotation 7) Sludge dewatering	8 000	2008

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used (^{1})	Unit operations (^{1})	Average waste water treated (10^3 m^3/yr)	Year
#36	DE	OFC	Direct, to a river	- Biological treatment using a membrane bioreactor - Nitrification/denitrification - Chemical phosphorus precipitation - Ultrafiltration for final solids removal	1) Screening 2) Neutralisation 3) Precipitation of phosphorus 4) Primary sedimentation 5) Biological treatment 6) Ultrafiltration	1 200	2007
#37	ES	SIC, LVOC, OFC, POL	Direct, to the sea	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sedimentation for final solids removal	1) Homogenisation 2) Aeration 3) Sedimentation 4) Sludge thickening	1 100	2011
#38	FR	SIC, OFC	Indirect, to a municipal WWTP	- Physico-chemical treatment only - Ultrafiltration for final solids removal	1) Decantation 2) Filtration 3) Ultrafiltration 4) Stripping with steam 5) Cooling	1.8	2007
#40	FR	OFC, POL	Direct, to a canal	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sedimentation for final solids removal	1) Equalisation 2) Flocculation and primary sedimentation 3) Activated sludge process 4) Denitrification 5) Secondary sedimentation 6) Sludge thickening	580	2011
#41	FR	OFC	Direct, to a river	- Biological treatment using activated sludge, and partially a membrane bioreactor - Nitrification/denitrification - Sedimentation/ultrafiltration for final solids removal	1) Equalisation 2) Neutralisation 3) Nitrification 4) Denitrification 5) Aeration 6) Sedimentation 7) Membrane bioreactor (ultrafiltration) for part of the effluent 8) Sludge dewatering	240	2007

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used (^{1})	Unit operations (^{1})	Average waste water treated (10^3 m^3/yr)	Year
#45	IT	LVIC-AAF, LVIC-S, LVOC, OFC, POL	Direct, to a river	- Biological treatment using activated sludge (tower biology) - Nitrification/denitrification - Sand filtration for final solids removal - Physico-chemical treatment for inorganic waste water - Sedimentation for final solids removal	- Treatment of organic waste water: 1) Screening 2) Oil-water separation (API) 3) Equalisation 4) Homogenisation and precipitation of metals 5) Neutralisation, coagulation, flocculation 6) Primary sedimentation 7) Air flotation 8) Tower biology 9) Sedimentation 10) Sand and activated carbon filtration - Treatment of inorganic waste water: 1) Screening 2) Sedimentation 3) Flocculation	11 000	2007
#46	IT	CAK, LVOC, POL	Indirect, to a biological WWTP	- Physico-chemical treatment only - Flotation for final solids removal	1) Oil-water separation (API) 2) Air flotation	5 800	2008
#47	ES	LVOC	Direct, to the sea	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	NI	600	2007
#48	ES	LVOC	Direct, to the sea	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Primary sedimentation 2) Primary sludge filtration 3) Aeration 4) Secondary sedimentation 5) Sludge digestion	2 900	2008
#49	BE	CAK, LVIC-AAF, LVOC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sedimentation for final solids removal	1) Sand grids 2) Aeration 3) Sedimentation 4) Sludge thickening	12 000	2011
#50	BE	LVIC-AAF, LVOC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Flotation for final solids removal	1) Neutralisation 2) Primary sedimentation 3) Denitrification 4) Aeration 5) Secondary sedimentation 6) Flotation 7) Cooling	4 000	2011

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used (^{1})	Unit operations (^{1})	Average waste water treated (10^3 m^3/yr)	Year
#51	BE	OFC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Chemical phosphorus precipitation - Flotation for final solids removal	1) Equalisation 2) Neutralisation and flocculation 3) Primary sedimentation 4) Aeration basin 5) Flotation 6) Sludge thickening (centrifugation)	270	2011
#52	BE	POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sedimentation for final solids removal	1) Equalisation 2) Denitrification 3) Aeration including nitrification 4) Sedimentation	120	2007
#53	BE	LVOC, POL	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Skimming 2) Archimedes screw for pellet removal 3) Sedimentation	430	2011
#54	BE	LVOC	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Equalisation 2) Aeration 3) Sedimentation 4) Waste gas treatment including active coal	3 900	2011
#56	DE	LVIC-S	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Equalisation 2) Neutralisation 3) Precipitation 4) Flocculation 5) Sedimentation	930	2007
#57	FR	OFC	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Chemical phosphorus precipitation - Sedimentation for final solids removal	1) Trickling bed as pretreatment of waste water without suspended solids 2) Primary sedimentation 3) Denitrification 4) Aeration 5) Secondary sedimentation	1 900	2007
#58	IT	LVIC-S, OFC, POL	Indirect, to a municipal WWTP	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Reverse osmosis for final solids removal	1) Equalisation 2) Neutralisation 3) Chemical precipitation 4) Oxidation with Fenton reagent 5) Biological treatment with activated sludge 6) Sedimentation 7) Filtration 8) Reverse osmosis 9) Mechanical sludge dewatering	35	2007

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used ([1])	Unit operations ([1])	Average waste water treated (10^3 m^3/yr)	Year
#60	FR	OFC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Flotation for final solids removal	1) Equalisation 2) Neutralisation 3) Primary sedimentation 4) Biological treatment 5) Secondary sedimentation 6) Flotation 7) Sludge thickening, conditioning, and dewatering	270	2008
#61	CZ	LVOC, OFC	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sand filtration for final solids removal	1) Equalisation 2) Three-stage aerobic biological treatment 3) Sedimentation 4) Sand filtration 5) Lagoon	970	2011
#62	CZ	LVOC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Equalisation 2) Two independent aeration stages 3) Sedimentation 4) Sludge dewatering	130	2007
#63	CZ	LVIC-AAF, LVOC, POL	Direct, to a river	- Biological treatment using activated sludge (flat tank) - Nitrification/denitrification - Sedimentation for final solids removal	1) Equalisation 2) Flocculation 3) Flotation 4) Denitrification 5) Aeration 6) Sedimentation	6 300	2011
#64	FR	LVOC, OFC, POL	Direct, to a lake	- Biological treatment using activated sludge (flat tank) - Flotation for final solids removal	1) Equalisation 2) Oil-water separation 3) Primary sedimentation 4) Neutralisation 5) Flocculation 6) Aeration 7) Secondary sedimentation 8) Coagulation, flocculation, and air flotation 9) Sludge dewatering	4 700	2007
#65	ES	OFC	Indirect, to a biological WWTP	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Chemical oxidation with hydroxide peroxide and iron 2) Neutralisation 3) Flocculation 4) Sedimentation 5) Sludge thickening	11	2007

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used (^{1})	Unit operations (^{1})	Average waste water treated (10^3 m^3/yr)	Year
#66	ES	POL	Indirect, to a municipal WWTP	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Chemical oxidation with hydroxide peroxide and iron 2) Neutralisation 3) Flocculation 4) Sedimentation 5) Sludge dewatering	2	2006
#67	ES	LVIC-S, OFC	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Equalisation and pH adjustment 2) Chemical oxidation with hydrogen peroxide and iron 3) Neutralisation and precipitation 4) Sedimentation 5) Sludge thickening (centrifugation)	450	2007
#68	AT	LVIC-AAF, LVOC, OFC	Indirect, to a municipal WWTP	- Biological treatment using activated sludge (flat tank) - Sedimentation for final solids removal	1) Equalisation and neutralisation 2) Two-stage aeration 3) Sedimentation	1 300	2008
#69	IT	CAK, LVIC-AAF, SIC, LVOC, POL	Direct, to the sea	- Biological treatment using a membrane bioreactor - Nitrification/denitrification - Ultrafiltration for final solids removal	1) Equalisation 2) Physico-chemical treatment 3) Activated sludge process 4) Ultrafiltration 5) Post-denitrification 6) Sludge treatment	9 100	2009
#70	AT	OFC	Direct, to a river	- Biological treatment using activated sludge, and partially a membrane bioreactor - Nitrification/denitrification - Chemical phosphorus precipitation - Sedimentation/ultrafiltration for final solids removal	Two stage-process for higher and lower contaminated waste water streams	2 800	2011
#73	DE	LVIC-AAF	Direct, to a river	Physico-chemical treatment only	1) Neutralisation 2) Precipitation of fluorides	1 900	2011
#74	DK	LVOC, OFC	Direct, to the sea	- Biological treatment - Nitrification/denitrification - Chemical phosphorus precipitation	1) Hydrolysis 2) Aeration/degradation 3) Neutralisation 4) Precipitation	950	2011

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used ([1])	Unit operations ([1])	Average waste water treated (10^3 m^3/yr)	Year
#75	DK	OFC	Direct, to a river	- Biological treatment using activated sludge - Nitrification/denitrification - Flotation for final solids removal	1) Activated sludge process 2) Sedimentation 3) Air flotation	160	2011
#76	DK	OFC	Indirect, to a municipal WWTP	- Biological treatment - Chemical phosphorus precipitation - Advanced oxidation process	NI	2 800	2011
#78	DK	OFC	Indirect, to a municipal WWTP	Physico-chemical treatment only	1) Oil-water separation	NI	2011
#79	ES	CAK, LVIC-S	Direct, to the sea	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Neutralisation 2) Coagulation, flocculation, precipitation 3) Sedimentation 4) Sludge dewatering	4 200	2011
#80	ES	CAK, LVOC	Direct, to the sea	Physico-chemical treatment only	1) Neutralisation 2) Homogenisation	1 600	2011
#81	ES	LVOC	Direct, to the sea	Physico-chemical treatment only	1) Activated carbon filtration 2) Neutralisation	NI	2011
#82	ES	LVIC-AAF, LVOC	Direct, to the sea	- Biological treatment - Nitrification/denitrification - Sedimentation for final solids removal	1) Biological treatment 2) Sedimentation	2 800	2011
#83	ES	LVOC, POL	Direct, to the sea	Biological treatment using activated sludge	1) Homogenisation 2) Screens and oil removal 3) Biological treatment	3 200	2011
#84	ES	LVIC-S, OFC	Direct, to a river	Physico-chemical treatment only	1) Advanced oxidation process with hydrogen peroxide 2) Neutralisation 3) Precipitation of metals	450	2007
#85	FR	POL	Direct, to a river	Physico-chemical treatment only	1) Grit separation 2) Oil-water separation (API) 3) Equalisation	NI	2011
#86	FR	POL	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Grit separation 2) Sedimentation	470	2010

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used ([1])	Unit operations ([1])	Average waste water treated (10³ m³/yr)	Year
#87	BE	POL	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Biological pretreatment in batch mode for waste water with high COD concentrations 2) Rotating filter 3) Tilted plate separator 4) Air flotation 5) Lagoon	560	2010
#88	IE	OFC	Indirect	NI	NI	82	2011
#89	IT	LVOC, POL	Direct, to the sea	- Biological treatment - Nitrification/denitrification - Sedimentation for final solids removal	1) Equalisation 2) Oil-water separation (API) 3) Flotation with nitrogen 4) Biological oxidation 5) Secondary sedimentation 6) Sludge thickening, dewatering and sterilisation	2 100	2011
#90	IT	LVOC	Direct, to the sea	- Biological treatment	1) Oil-water separation (API and TPI) 2) Biological treatment	710	2011
#91	IT	LVOC, POL	Direct, to a river	- Biological treatment using activated sludge - Sedimentation for final solids removal	1) Equalisation 2) Two active sludge reactors 3) Degasification 4) Sedimentation 5) Sludge thickening	9 200	2011
#92	PL	LVIC-S, LVIC-AAF, LVOC	Direct, to a river	- Biological treatment - Nitrification/denitrification	NI	7 200	2011
#93	PL	LVIC-AAF, POL	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Neutralisation 2) Coagulation 3) Sedimentation	3 900	2011
#94	PL	LVIC-AAF	Direct, to a river	- Physico-chemical treatment only - Sedimentation for final solids removal	1) Neutralisation 2) Sedimentation	950	2011
#95	PL	LVIC-AAF, LVIC-S	Direct, to a river	Physico-chemical treatment only	Includes chemical phosphorus precipitation	27 000	2011
#96	PL	LVIC-AAF, LVOC	Direct, to a river	- Biological treatment using activated sludge - Nitrification/denitrification	1) Primary sedimentation 2) Flotation 3) Activated sludge process	2 400	2011
#98	PL	SIC, LVOC, POL	Direct, to a river	- Biological treatment - Nitrification/denitrification	NI	13 000	2011
#100	SE	OFC	Direct, to a lake	- Biological treatment - Nitrification/denitrification - Sedimentation for final solids removal	1) Primary sedimentation 2) Denitrification 3) Aerobic treatment 4) Secondary sedimentation	1 700	2010

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used (^{1})	Unit operations (^{1})	Average waste water treated (10^3 m^3/yr)	Year
#101	SE	LVOC	Direct, to the sea	Biological treatment	NI	330	2010
#102	SE	LVOC	Direct, to the sea	Biological treatment using activated sludge	NI	800	2010
#103	SE	LVOC	Direct, to the sea	Biological treatment using activated sludge	NI	180	2010
#104	SE	LVOC	Direct, to a river	Biological treatment using activated sludge	NI	650	2010
#105	UK	SIC	Direct, to a river	- Biological treatment - Filtration for final solids removal	1) Bioreactors 2) Sedimentation 3) Filtration	1 800	2011
#106	UK	LVOC	Direct, to an estuary	Physico-chemical treatment only	Neutralisation	41	2011
#107	UK	OFC	Direct, to an estuary	Physico-chemical treatment only	1) Equalisation 2) Neutralisation	NI	2011
#108	UK	OFC	Direct, to an estuary	- Biological treatment using activated sludge - Nitrification/denitrification	Two-stage biological treatment	2 000	2011
#109	UK	OFC	Direct, to the sea	Physico-chemical treatment only	1) Equalisation 2) Neutralisation	310	2011
#110	UK	OFC	Direct, to an estuary	Physico-chemical treatment only	1) Equalisation 2) Neutralisation	NI	2011
#111	UK	LVOC	Direct, to an estuary	Physico-chemical treatment only	Neutralisation	4 400	2011
#113	UK	POL	Direct, to a river	Physico-chemical treatment only	Neutralisation	640	2011
#114	UK	OFC	Direct, to an estuary	Physico-chemical treatment only	Dilution	100	2011
#115	UK	SIC	Direct, to an estuary	- Physico-chemical treatment only - Sand filtration for final solids removal	1) Neutralisation 2) Sedimentation 3) Coagulation and flocculation 4) Air flotation 5) Sand filtration	5 400	2011
#116	UK	SIC	Direct, to an estuary	Physico-chemical treatment only	1) Neutralisation 2) Dilution	NI	2011
#117	UK	LVIS-S	Direct, to a river	- Physico-chemical treatment only - Filtration for final solids removal	1) Neutralisation 2) Sedimentation 3) Filtration	12	2011

WWTP code	Location	IED chemical installations at the site	Discharge type	Main techniques used ([1])	Unit operations ([1])	Average waste water treated (10^3 m^3/yr)	Year
#118	FR	OFC	Direct, to a river	- Biological treatment using membrane bioreactor - Nitrification/denitrification - Ultrafiltration for final solids removal	1) Stripping 2) Sedimentation 3) Membrane bioreactor	330	2011
#119	FR	LVIC-AAF	Direct	No final treatment	No final treatment	2 100	2011
#120	FR	LVIC-AAF	Direct	- Physico-chemical treatment only - Sand filtration for final solids removal	1) Neutralisation 2) Sand filtration	440	2011
#121	UK	LVIC-S	Direct, to an estuary	Physico-chemical treatment only	Neutralisation	7 800	2011

([1]) The information contained in this column might be incomplete.

NB: NI = no information provided.

Source: [222, CWW TWG 2013]

7.3   Annex III. Example of EMFA: 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 these processes – the optimisation of water consumption and waste discharge – are within the scope of this BREF. Optimisation of production processes is covered by the other chemical BREFs and other references [251, Ullmann's 2000].

Pinch technology is a methodology for optimising the use of consumables in processes and on sites by introducing process-integrated 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. The concept of pinch technology is to define and find potential water savings, e.g. by 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 redesign distributed effluent treatment so as to lower investment costs by reducing the hydraulic load of a central WWTP.

Its application can be broken down into four steps [26, Linnhoff et al. 1998]:

Step 1:
- Drawing a flow sheet 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.

Source: [26, Linnhoff et al. 1998]
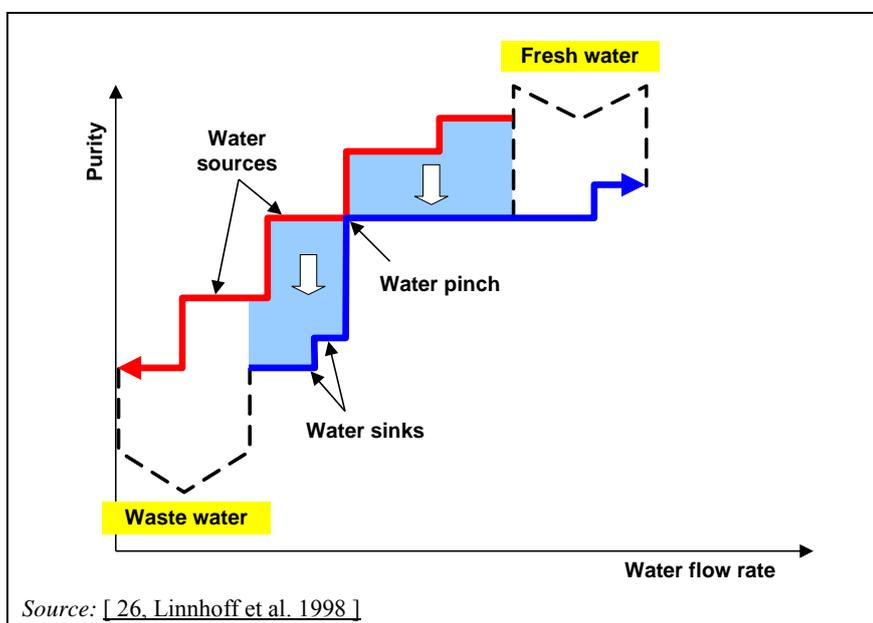
Figure 7.3:   Pinch technology – analysis, source and sink curves

Step 2:
- Selecting key contaminants or properties that prevent the direct reuse 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 achieving waste water savings of up to 60 % [26, Linnhoff et al. 1998]. Performance examples for waste water flow reduction are:

- chemicals and fibres25 %
- chemicals40 %
- coal chemicals50 %
- polymers60 %.

An example of a water conservation strategy is given in Figure 7.4.

Source: [26, Linnhoff et al. 1998]
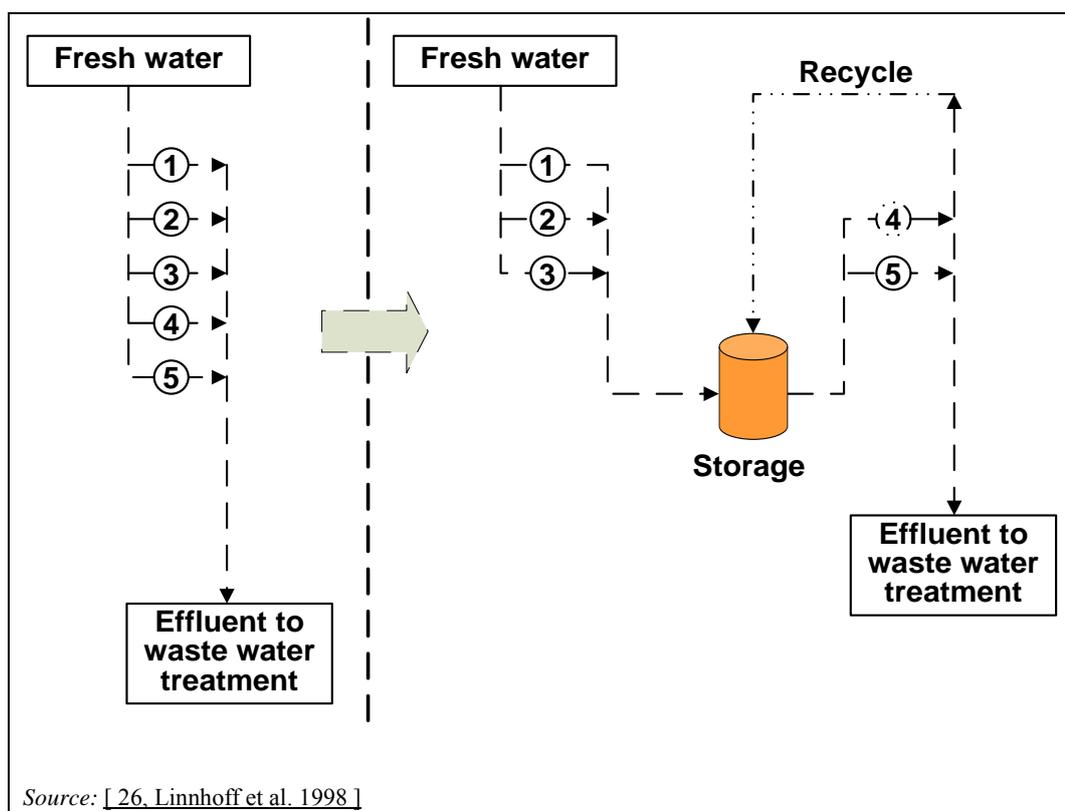
Figure 7.4:   Example of a water conservation strategy before and after pinch analysis

Cost savings are not normally restricted to water cost savings. 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 [26, Linnhoff et al. 1998] include:

- to avoid production cutbacks under limited water supply conditions;
- to reduce water supply costs;
- to reduce investment costs of new water supply facilities (e.g. new wells or pipelines);
- to reduce investment costs of water treatment facilities;
- to reduce waste water treatment costs;
- to reduce sewerage charges;
- to reduce investment 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.

7.4   Annex IV. Pollution incident response plan

An example of a pollution incident response plan, as mentioned in Section 3.1.5.5.3, is detailed here. The information asked for is generally applicable to all sites. Special productions or site-specific features might require further information.

Source: [75, Environmental Alliance (UK) 2000]

Figure 7.5:   Pollution incident response plan

GLOSSARY

This glossary is meant to facilitate the understanding of the information contained in this document. The definitions of terms in this glossary are not legal definitions (even if some of them may coincide with definitions given in European legislation), they are meant to help the reader understand some key terms in the context of their use in the specific sector covered by this document.

This glossary is divided up into the following sections:

I.ISO country codes
II.Monetary units
III.Unit prefixes
IV.Units
V.Chemical elements
VI.Chemical formulae and substances commonly referred to in this document
VII.Acronyms commonly used in this document
VIII.Terms commonly used in this document

I. ISO country codes

ISO code	Country
Member States (*)	
BE	Belgium
CZ	Czech Republic
DK	Denmark
DE	Germany
IE	Ireland
ES	Spain
FR	France
IT	Italy
HU	Hungary
NL	Netherlands
AT	Austria
PL	Poland
PT	Portugal
FI	Finland
SE	Sweden
UK	United Kingdom
Non-member countries	
US	United States
(*) The protocol order of the Member States is based on the alphabetical order of their geographical names in the original language(s).	

II. Monetary units

Code([1])	Country/territory	Currency
Member State currencies		
EUR	Euro area ([2])	euro (pl. euros)
ATS	Austria	Austrian schilling
DEM	Germany	German mark
FIM	Finland	Finnish markka
GBP	United Kingdom	pound sterling (inv.)
NLG	Netherlands	Dutch guilder
Other currencies		
USD	United States	US dollar

([1]) ISO 4217 codes.
([2]) Includes Austria, Belgium, Cyprus, Estonia, Finland, France, Germany, Greece, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, the Netherlands, Portugal, Slovakia, Slovenia, Spain.

III. Unit prefixes

Symbol	Prefix	Term	Number
E	exa	10^{18}	1 000 000 000 000 000 000
P	peta	10^{15}	1 000 000 000 000 000
T	tera	10^{12}	1 000 000 000 000
G	giga	10^{9}	1 000 000 000
M	mega	10^{6}	1 000 000
k	kilo	10^{3}	1 000
h	hecto	10^{2}	100
da	deca	10^{1}	10
-------	-------	1 unit	1
d	deci	10^{-1}	0.1
c	centi	10^{-2}	0.01
m	milli	10^{-3}	0.001
μ	micro	10^{-6}	0.000 001
n	nano	10^{-9}	0.000 000 001

IV. Units

Term	Meaning
Am^3	actual m^3 (cubic metre for gases, measured at the pressure and temperature conditions stated). m^3 has the same meaning and is used more often than Am^3
bar	bar (1.013 bar = 100 kPa)
billion	1 000 million
°C	degree Celsius, centigrade
cm	centimetre
d	day
g	gram
gal	gallon (1 gal = 3.785 l)
h	hour
ha	hectare
J	joule (1 J = 0.239 cal)
K	kelvin (0 °C = 273.15 K)
kg	kilogram
kPa	kilopascal (1 kPa = 10 mbar)
kt	kilotonne
kWh	kilowatt-hour (1 kWh = 3.6 MJ)
l	litre (1 l = 0.001 m^3)
m	metre
m^2	square metre
m^3	cubic metre
mg	milligram (1 mg = 10^{-3} g)
min	minute
MJ	megajoule (1 MJ = 239 kcal = 0.277 8 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)
ou_E	European odour unit (as defined by EN 13725). It is the unit of measurement for odour concentration. 1 ou_E corresponds to the amount of odorants which, diluted in one cubic metre of neutral air, produces a barely perceptible olfactory physiological response (1 ou_E/m^3 is the odour concentration corresponding to the olfactory threshold)
Pa	pascal (pressure; 1 Pa = 1 N/m^2)
ppb	parts per billion (1 ppb = 10^{-9})
ppbv	parts per billion by volume
ppm	parts per million (1 ppm = 10^{-6})
ppmw	parts per million (by weight)
ppmv	parts per million (by volume) (ppm × molecular weight/22.41 = mg/Nm^3; 1 ppm NO_2 = 2.05 mg/Nm^3 NO_2)
s	second
S	siemens
t	metric tonne (1 t = 1 000 kg)
t/d	tonnes per day
t/yr	tonnes per year
TEQ	toxicity equivalents of dioxins
vol-%	percentage by volume
wt-%	percentage by weight
W	watt (1 W = 1 J/s)
yr	year
Ω	ohm

V. Chemical elements

Symbol	Name	Symbol	Name
Ac	Actinium	Mn	Manganese
Ag	Silver	Mo	Molybdenum
Al	Aluminium	N	Nitrogen
Am	Americium	Na	Sodium
Ar	Argon	Nb	Niobium
As	Arsenic	Nd	Neodymium
At	Astatine	Ne	Neon
Au	Gold	Ni	Nickel
B	Boron	No	Nobelium
Ba	Barium	Np	Neptunium
Be	Beryllium	O	Oxygen
Bi	Bismuth	Os	Osmium
Bk	Berkelium	P	Phosphorus
Br	Bromine	Pa	Protactinium
C	Carbon	Pb	Lead
Ca	Calcium	Pd	Palladium
Cd	Cadmium	Pm	Promethium
Ce	Cerium	Po	Polonium
Cf	Californium	Pr	Praseodymium
Cl	Chlorine	Pt	Platinum
Cm	Curium	Pu	Plutonium
Co	Cobalt	Ra	Radium
Cr	Chromium	Rb	Rubidium
Cs	Caesium	Re	Rhenium
Cu	Copper	Rf	Rutherfordium
Dy	Dysprosium	Rh	Rhodium
Er	Erbium	Rn	Radon
Es	Einsteinium	Ru	Ruthenium
Eu	Europium	S	Sulphur
F	Fluorine	Sb	Antimony
Fe	Iron	Sc	Scandium
Fm	Fermium	Se	Selenium
Fr	Francium	Si	Silicon
Ga	Gallium	Sm	Samarium
Gd	Gadolinium	Sn	Tin
Ge	Germanium	Sr	Strontium
H	Hydrogen	Ta	Tantalum
He	Helium	Tb	Terbium
Hf	Hafnium	Tc	Technetium
Hg	Mercury	Te	Tellurium
Ho	Holmium	Th	Thorium
I	Iodine	Ti	Titanium
In	Indium	Tl	Thallium
Ir	Iridium	Tm	Thulium
K	Potassium	U	Uranium
Kr	Krypton	V	Vanadium
La	Lanthanum	W	Tungsten
Li	Lithium	Xe	Xenon
Lr	Lawrencium	Y	Yttrium
Lu	Lutetium	Yb	Ytterbium
Md	Mendelevium	Zn	Zinc
Mg	Magnesium	Zr	Zirconium

VI. Chemical formulae and substances commonly referred to in this document

Chemical formula	Name
Al^{3+}	Aluminium(III) ion
Al_2O_3	Aluminium oxide
Br_2	Bromine
Ca^{2+}	Calcium(II) ion
$CaCO_3$	Calcium carbonate
$Ca(HSO_3)_2$	Calcium hydrogen sulphite / Calcium bisulphite
CaO	Calcium oxide
$CaSO_3$	Calcium sulphite
$CaSO_4$	Calcium sulphate
$CaSO_4 \cdot 2\,H_2O$	Calcium sulphate dihydrate (gypsum)
$Ca(OH)_2$	Calcium hydroxide (lime)
Cd^{2+}	Cadmium(II) ion
CH_4	Methane
$C_{13}H_{14}N_4O$	1,5-Diphenylcarbazide
$((CH_3)_3SiCN)$	Trimethylsilyl cyanide
Cl^-	Chloride ion
Cl_2	Chlorine
ClO_2	Chlorine dioxide
CN^-	Cyanide ion
CO	Carbon monoxide
CO_2	Carbon dioxide
COS	Carbon oxysulphide
Cr^{3+}	Chromium(III) ion
CrO_4^{2-}	Chromate ion
CS_2	Carbon disulphide
Cu^{2+}	Copper(II) ion
C_XH_Y	Hydrocarbons
F^-	Fluoride ion
Fe^{2+}	Iron(II) ion / Ferrous ion
Fe^{3+}	Iron(III) ion / Ferric ion
H_2	Hydrogen
H_3BO_3	Boric acid
HBr	Hydrogen bromide
HCl	Hydrogen chloride / Hydrochloric acid
HCN	Hydrogen cyanide
HF	Hydrogen fluoride
HI	Hydrogen iodide
HNO_3	Nitric acid
H_2O	Water
H_2O_2	Hydrogen peroxide
HPO_4^{2-}	Hydrogen phosphate ion
$H_2PO_4^-$	Dihydrogen phosphate ion
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
KCN	Potassium cyanide
$KMnO_4$	Potassium permanganate

Chemical formula	Name
MnO_2	Manganese dioxide
N_2	Nitrogen
$NaCN$	Sodium cyanide
Na_2CO_3	Sodium carbonate, soda
$NaHCO_3$	Sodium hydrogen carbonate / Sodium bicarbonate
$NaHSO_3$	Sodium hydrogen sulphite
$NaNO_3$	Sodium nitrate
$NaOCl$	Sodium hypochlorite
$NaOH$	Sodium hydroxide
Na_2S_4	Disodium tetrasulphide
$NCBr$	Cyanogen bromide
$NCCl$	Cyanogen chloride / Chlorocyan
NH_3	Ammonia
NH_4^+	Ammonium ion
NH_4Cl	Ammonium chloride
NH_2CN	Cyanamide
$(NH_2)_2CO$	Urea
Ni^{2+}	Nickel(II) ion
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 NO_2)
O_2	Oxygen
O_2^-	Superoxide ion
O_3	Ozone
OCl^-	Hypochlorite ion
OCN^-	Cyanate ion
PO_4^{3-}	Phosphate ion
RuO_2	Ruthenium dioxide
S^{2-}	Sulphide ion
SCN^-	Thiocyanate ion
$SC(NH_2)_2$	Thiourea
SiO_2	Silicon dioxide
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)
TiO_2	Titanium dioxide
Zn^{2+}	Zinc(II) ion

VII. Acronyms commonly used in this document

Acronym	Definition
A/C ratio	Airflow to cloth area ratio
ADEME	Agence de l'Environnement et de la Maîtrise de l'Énergie (French Environment and Energy Management Agency)
AOX	Adsorbable organically bound halogens. AOX, expressed as Cl, include adsorbable organically bound chlorine, bromine and iodine
API	American Petroleum Institute. API separators are commonly used oil-water separators
ARIA	Analyse, Recherche et Information sur les Accidents (Analysis, research and information on accidents)
ATEX Directives	EU directives related to the manufacture and use of equipment in an explosive atmosphere. ATEX derives its name from the French title of Directive 94/9/EC: 'Appareils destinés à être utilisés en ATmosphères EXplosibles'.
BARPI	Bureau of Risk Analysis and Industrial Pollution
BAT	Best available techniques, as defined in Article 3(10) of the IED
BMU	Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit (German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety)
BOD_X	Biochemical oxygen demand in X days. Amount of oxygen needed for the biochemical oxidation of the organic matter to carbon dioxide in X days (normally 5 or 7). BOD is an indicator for the mass concentration of biodegradable organic compounds.
BREF	Best available techniques reference document
BTEX	Benzene, toluene, ethylbenzene, xylene
CAK BREF	BREF for the Production of Chlor-alkali
CASQA	California Stormwater Quality Association
CEFIC	European Chemical Industry Council (from its French name Conseil Européen des Fédérations de l'Industrie Chimique)
CEN	European committee for standardisation (from its French name Comité Européen de Normalisation)
CER BREF	BREF Document for the Ceramic Manufacturing Industry
CFA	Continuous flow analysis
CMAS	Complete mix activated sludge
COD	Chemical oxygen demand. Amount of oxygen needed for the total oxidation of organic matter to carbon dioxide. COD is an indicator for the mass concentration of organic compounds
COM	European Commission
CPI	Corrugated plate interceptor
CWW BREF	BREF on Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector
DAF	Dissolved air flotation
DDT	Dichlorodiphenyltrichloroethane / 1,1,1-Trichloro-2,2-bis-(*p*-chlorophenyl)ethane; a pesticide
DEFRA	Department for Environment, Food and Rural Affairs (UK)
DGF	Dissolved gas flotation
DIAL	Differential absorption LIDAR
DOC	Dissolved organic carbon
EC	European Communities
EC_X	Effluent concentration in dilution water that causes a measurable negative effect on X % of the test population
EC_{50}	Effluent concentration in dilution water that causes a measurable negative effect on 50 % of the test population
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECM REF	Reference Document on Economics and Cross-Media Effects
EDTA	Ethylenediaminetetraacetic acid
EEC	European Economic Community
EFS BREF	BREF on Emissions from Storage
EHS	Environment, health and safety
EIPPCB	European Integrated Pollution Prevention and Control Bureau
EMAS	Eco-Management and Audit Scheme (Council Regulation EC/761/2001)
EMFA	Energy and material flow analysis

Acronym	Definition
EMS	Environmental Management System
EOX	Extractable organically bound halogens
E-PRTR	European Pollutant Release and Transfer Register
ESA	European Sealing Association
ESP	Electrostatic precipitator
ETBPP	Environmental Technology Best Practice Programme
EU	European Union
FGD	Flue-gas desulphurisation
FIA	Flow injection analysis
FID	Flame ionisation detector
FRP	Fibreglass-reinforced plastic
GAC	Granular activated carbon
GC	Gas chromatography
HAP	Hazardous air pollutants
HEAF	High-efficiency air filter
HEL	Higher explosive limit
HEPA filter	High-efficiency particle air filter
HEPES	4-(2-hydroxyethyl)-1-piperazineethanesulphonic acid
HMIP	Her Majesty's Inspectorate of Pollution
IAF	Induced air flotation **or** International Accreditation Forum
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
ICS BREF	BREF for Industrial Cooling Systems
IED	Industrial Emissions Directive
IGF	Induced gas flotation
IMPEL	European Union Network for the Implementation and Enforcement of Environmental Law
INERIS	Institut National de l'Environnement Industriel et des Risques (French National Institute for Industrial Safety and Environmental Protection)
InfoMil	Dutch Information Centre for Environmental Licensing
IPPC	Integrated Pollution Prevention and Control
ISO	International Organization for Standardization
LANUV NRW	Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen (Agency for Nature, Environment, and Consumer Protection of the German State of North Rhine-Westphalia)
LAWA	Bund/Länder-Arbeitsgemeinschaft Wasser (German Working Group on water issues of the Federal States and the Federal Government)
LCP BREF	BREF for Large Combustion Plants
LC_X	Effluent concentration in dilution water that causes mortality in X % of the test population
LC_{50}	Effluent concentration in dilution water that causes mortality in 50 % of the test population
LDAR	Leak detection and repair
LEL	Lower explosive limit
LID	Lowest ineffective dilution; numeric value given as reciprocal dilution value (dimensionless) of the waste water at which no effects are observed
LIDAR	Light detection and ranging
LLA	Lower limit of application
LLE	Liquid/liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
LVIC-AAF BREF	BREF for the Manufacture of Large Volume Inorganic Chemicals - Ammonia, Acids, Fertilisers
LVIC-S BREF	BREF for the Manufacture of Large Volume Inorganic Chemicals - Solids and Others Industry (LVIC-S BREF)
LVOC	Large volume organic chemicals
LVOC BREF	BREF for the Large Volume Organic Chemicals Industry
MBR	Membrane bioreactor
MF	Microfiltration (membrane process, waste water section)
MGD	Million gallons per day

Acronym	Definition
MTBE	Methyl *tert*-butyl ether
NMVOC	Non-methane volatile organic compounds
MS	Mass spectrometry
NF	Nanofiltration (membrane process, waste water section)
NH_4-N	Ammonium (calculated as N)
N_{inorg}	Total inorganic nitrogen. N_{inorg}, expressed as N, includes free ammonia and ammonium (NH_4-N), nitrites (NO_2-N) and nitrates (NO_3-N)
NOAEC	No observed adverse effect concentration
NO_2-N	Nitrite (calculated as N)
NO_3-N	Nitrate (calculated as N)
NOREC	North Ostrobothnia Regional Environment Centre (FI)
NSCR	Non-selective catalytic reduction
OFC	Organic fine chemicals
OFC BREF	BREF for the Manufacture of Organic Fine Chemicals
OSPAR	Oslo and Paris Convention for the Protection of the Marine Environment of the North-East Atlantic
PAC	Powdered activated carbon
PAH	Polycyclic aromatic hydrocarbon
PBT	Persistent, liable to bioaccumulation and/or toxic
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxin
PCDF	Polychlorinated dibenzofuran
p.e.	Population equivalent, means the organic biodegradable load having a five-day biochemical oxygen demand (BOD_5) of 60 g of oxygen per day
PFOS	Perfluorooctane sulphonate
PID	Photo-ionisation detector
PM	Particulate matter
PM_X	Particulate matter suspended in air which is small enough to pass through a size-selective inlet with a 50 % efficiency cut-off at X μm aerodynamic diameter
POL BREF	BREF for the Production of Polymers
PO_4-P	Phosphate (calculated as P)
PPI	Parallel plate interceptor
PSA	Pressure-swing adsorption
PTFE	Polytetrafluoroethene (Teflon)
PVC	Polyvinyl chloride
RADAR	Radio detection and ranging
RO	Reverse osmosis (membrane process, waste water section)
ROM REF	JRC Reference Report on Monitoring of Emissions to Air and Water from IED installations
SCA	Specific collection area (ESP: ratio of surface area of collection electrodes to gas flow: e.g. $m^2/(m^3/s)$ or s/m)
SCR	Selective catalytic reduction (NO_X reduction)
SCWO	Supercritical water oxidation
SEPA	Scottish **or** Swedish Environmental Protection Agency
SIC BREF	BREF for the production of Speciality Inorganic Chemicals
SMEs	Small and medium-sized enterprises
SNCR	Selective non-catalytic reduction (NO_X reduction)
SOF	Solar occultation flux
SPC	Statistical process control
SPME	Solid-phase microextraction
SVI	Sludge volume index: Volume in ml occupied by 1 g of activated sludge after settlement under specified conditions for a specified time
TCEQ	Texas Commission on Environmental Quality
TKN	Total Kjehldahl nitrogen. TKN, expressed as N, includes free ammonia and ammonium (NH_4-N) and organic nitrogen compounds
TN	Total nitrogen. TN, expressed as N, includes free ammonia and ammonium (NH_4-N), nitrites (NO_2-N), nitrates (NO_3-N) and organic nitrogen compounds
TOC	Total organic carbon. TOC, expressed as C, includes all organic compounds
TSS	Total suspended solids. Mass concentration of all suspended solids, measured via filtration through glass fibre filters and gravimetry

Acronym	Definition
TP	Total phosphorus. TP, expressed as P, includes all inorganic and organic phosphorus compounds, dissolved or bound to particles
TU	Toxic unit
TU_a	Acute toxic unit: equals $100/EC_{50}$
TU_c	Chronic toxic unit: equals 100/NOAEC or LID
TWG	Technical working group. Group of experts composed of representatives from Member States, the industries concerned, non-governmental organisations promoting environmental protection and the Commission for the drawing up and review of BREFs
UASB process/reactor	Upflow anaerobic sludge blanket process/reactor
UBA AT	Umweltbundesamt (Austrian Federal Environment Agency)
UBA DE	Umweltbundesamt (German Federal Environment Agency)
UF	Ultrafiltration
ULPA filter	Ultra-low penetration air filter
UNSW	University of New South Wales (Australia)
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
VCI	Verband der Chemischen Industrie e.V (Association of the German chemical industry)
VDI	Verein Deutscher Ingenieure (Association of German Engineers)
VFA	Volatile fatty acids
VITO	Vlaamse Instelling voor Technologisch Onderzoek (Flemish Institute for Technological Research)
VOC	Volatile organic compound as defined in Article 3(45) of the IED
VOX	Volatile organically bound halogens
VRU	Vapour recovery unit
WEA	Whole effluent assessment
WEF	Water Environment Federation
WI BREF	BREF for Waste Incineration
WT BREF	BREF for the Waste Treatments Industries
WWTP	Waste water treatment plant

VIII. Terms commonly used in this document

Terms used	Definition
Aerobic processes	Biological processes that occur in the presence of oxygen
Anaerobic processes	Biological processes that occur in the absence of any common electron acceptor such as nitrate, sulphate or oxygen
Anoxic processes	Biological processes that occur in the presence of electron acceptors such as nitrate or sulphate, while oxygen is absent
Biodegradability	Extent to which an organic substance can be degraded by microorganisms under specified conditions. Biodegradability is usually expressed as a percentage of the substance degraded
Biological nutrient removal	Removal of nitrogen and phosphorus in biological treatment processes
Colloids	Very small, finely divided solids that remain dispersed in a liquid for a long time due to their small size and electrical charge. When most of the particles in water have a negative electrical charge, they tend to repel each other, thereby preventing them from coagulating and sedimenting
Common techniques	Techniques that are ordinarily/frequently used or applicable within the chemical industry sector
Cross-media effects	Relevant negative environmental effects due to the implementation of a technique [232, EU 2012]
Diffuse VOC emissions	Non-channelled VOC emissions which can result from 'area' sources (e.g. tanks) or 'point' sources (e.g. pipe flanges)
Dilution factor	Reciprocal value of the volume fraction of waste water in dilution water in which a toxicity test is carried out (example: 250 ml of waste water in a total volume of 1 l represent a dilution factor of 4)
Dust	Total particulate matter (in air)
Effluent	Waste stream (waste water or waste gas) discharged from a process, an installation or a site
Elution	The process of extracting a substance that is adsorbed to another by washing it with a solvent. The substance used as a solvent in elution is called an eluent. The solution of the solvent and the substance that was adsorbed to another is called the eluate
Emission	Direct or indirect release of substances, vibrations, heat or noise from individual or diffuse sources in the installation into air, water or land (Article 3(4) of the IED)
Emission limit value	The mass, expressed in terms of certain specific parameters, concentration and/or level of an emission, which may not be exceeded during one or more periods of time (Article 3(5) of the IED)
Exhaust air	Waste gas from an installation contaminated with gaseous compounds, normally with low concentrations
End-of-pipe technique	A technique that reduces final emission or consumption levels but which does not change the fundamental operation of the core process. Synonyms are 'secondary technique' and 'abatement technique'; antonyms are 'primary technique' and 'process-integrated technique' (i.e. a technique that in some way changes the way in which the core process operates thereby reducing raw emission or consumption levels)
Flue-gas	Waste gas generated by a combustion/incineration process
Fugitive VOC emissions	Diffuse VOC emissions from 'point' sources
Halogenated organic compound	An organic compound which contains at least one atom of bromine, chlorine, fluorine or iodine per molecule
Heavy metals	Metals with a density greater than 4.5 g/ml
Installation	Stationary technical unit within which one or more activities listed in Annex I to the IED or in Part 1 of Annex VII to the IED are carried out, and any other directly associated activities on the same site which have a technical connection with the activities listed in those Annexes and which could have an effect on emissions and pollution (Article 3(3) of the IED)
Limit of detection	Lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated confidence limit (often with a confidence of 95 %)
Make-up water	Water added to a process to start or maintain a reaction, prepare a solution, mix reactants, or to dilute reactants

Terms used	Definition
Mineralisation	Conversion of an organic substance to inorganic substances (e.g. CO_2, water, ammonia in aerobic mineralisation) as a consequence of microbial activity
Mist	A suspension of fine drops of a liquid in a gas
Mother liquor	Waste water stream directly arising from a synthesis or chemical reaction, generally containing high concentrations of products, starting material or side products
Odour	Odour can be defined as a perception involving a set of complex processes (neurosensory process, cognitive process and amnesic process). This perception results from interactions between the olfactory mucosa (located in the nasal cavity) and gaseous substances, in particular volatile organic compounds (VOCs) [195, ADEME 2009]
Odour concentration	The concentration of an odorant mixture is conventionally defined as the dilution factor to be applied to an effluent in order to be no longer perceived as odorant by 50 % of people in a sample of the population. The odour concentration at the limit of detection is by definition 1 ou_E/m^3 [195, ADEME 2009]
Odour intensity	Value of the perception for a stimulus above the corresponding detection threshold. The odour intensity is determined by a sample of persons by comparing the odour perception level in the effluent with samples of an odorant reference (butanol at different levels of dilution) [195, ADEME 2009]
Odour threshold	The limiting concentration of a substance in air below which its odour is not perceptible [197, DEFRA 2010]
Particulate matter	A collective name for all solid or liquid particles suspended in air including dust, smoke, soot, pollen and soil particles. This complex mixture includes both organic and inorganic particles and varies greatly in size distribution, composition and origin. Based on size, particulate matter is often divided into two main groups. The coarse fraction contains the larger particles with a size ranging from 2.5 to 10 µm ($PM_{2.5-10}$). The fine fraction contains the smaller ones with a size up to 2.5 µm ($PM_{2.5}$). The particles in the fine fraction which are smaller than 0.1 µm ($PM_{0.1}$) are called ultrafine particles
Process water	Process water covers the wide range of boiler feed water, cooling water for heat exchangers or engines, chemicals dilution, etc.
Refractory TOC or COD	Organic fraction of pollutants in waste waters that are not amenable to being easily degraded in conventional biological treatment (whereas the COD tests shows they are chemically oxidisable) and/or exhibit a low value for the ratio of biological oxygen demand to chemical oxygen demand (BOD/COD)
Stoichiometric ratio	Ratio between the quantity of a reactant used in a reaction and the stoichiometric quantity necessary for the reaction to be complete
Substance	Chemical element and its compounds, with the exception of radioactive substances, genetically modified microorganisms and genetically modified organisms (Article 3(1) of the IED)
Substantial change	Change in the nature or functioning, or an extension, of an installation which may have significant negative effects on human health or the environment (Article 3(9) of the IED)
Volatile organic compound	Any organic compound as well as the fraction of creosote, 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 (Article 3(45) of the IED)
Zeolites	Aluminosilicate minerals that have a microporous structure (pores smaller than 2 nm)

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