Convention on Long-Range Transboundary Air Pollution

50<sup>th</sup> Working Group on Strategies and Review – 10 to 14 September 2012

Prepared by EGTEI

# Guidance document on control techniques for emissions of sulphur, NOx, VOCs, dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and black carbon) from stationary sources

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AEL	Associated Emission Levels	
ACI	Activated carbon injection	
Am <sup>3</sup>	Actual m <sup>3</sup>	
AS	Air staging	
<u>ASK</u>	Annular shaft kiln	
BAT	Best Available Techniques	
<u>BBF</u>	Biased Burner Firing	
<u>3C</u>	Black Carbon	
BF	Blast furnace	
BOF	Basic oxygen furnace	
<u>3005</u>	Burners Out of Service	
Bra	Brown Carbon	Mis en forme : Anglais (Royaume-
BREF	Best available technique reference document	
BTEX	Benzene, toluene, ethylbenzene, and xylenes	
°C	Celsius degree	
C eq	Carbon equivalent	
CaO	Calcium oxide	
CaCO₃	Calcium carbonate	
<u>Ca(OH)<sub>2</sub></u>	Calcium hydroxide	
<u></u>	Carbon ion	
CCGT	Combined Cycle Gas Turbines	
CCS	Carbon capture and storage	
CDQ	Coke dry quenching	
CFBC	Circulating fluidised-bed combustion	
CFA	Circulating fluidised-bed absorber	
СНР	Combined Heat and Power	
COG	Coke Oven Gas	
COHPAC™	Compact Hybrid Particulate Collector	
CONCAWE	European Oil Company Organisation for Environment, Health and Safety	
Co	Cobalt	
00	Carbon Monoxide	
$CO_2$	Carbon Dioxide	
00C	Condensable organic compounds	
CPIV	Comité Permanent des Industries du Verre de la CEE	
Cr	Chromium	Mis en forme : Anglais (États Unis
Cu	Copper	
DF	Dual Fuel	
DLN	Dry low NO <sub>x</sub>	
OPF	Diesel Particulate Filters	
DRI	Direct Reduced Iron	
E/kW	Euro per Kilo watt	
£/kWh	Euro per Kilo Watt hour	
E/ton	Euro per ton	
EAF	Electric arc furnace	
<u>-AF</u> JNECE		Mis en forme : Anglais (États Unis
<u>EED</u>	United Nations Economic Commission for Europe Energy efficient design	

EGR	Exhaust gas recirculation	
ELV	Emission Limit Value	
EMEP	European Monitoring and Evaluation Programme under the Convention on	
	Long-Range Transboundary Air Pollution (LRTAP)	
ESP	Electrostatic precipitator	
FBC	Fluidized bed combustion	
FCC	Fluid Catalytic Cracking	
Fe	Iron	
FF	Fabric filter	
FGD	Flue gas desulphurisation	
FGR	Flue Gas Recirculation	Mis en forme : Anglais (États Unis)
<u>FR</u>	Fuel re-burning	
FS	Fuel staging	
GD	Gas Diesel	Mis en forme : Anglais (États Unis)
GHG	Greenhouse Gases	
GJ	Giga Joule	
GSA	Gas suspension absorber	Mis en forme : Anglais (États Unis)
HCI	Hydrochloric Acid	
H <sub>2</sub> S	Hydrogen sulphide	
HEPA	High efficiency particulate air filter	
HF	Hydrogen fluoride	
HFO	Heavy Fuel Oil	
H <sub>2</sub>	Hydrogen	
Hg	Mercury	
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid	
IFC	International Finance Corporation	
IGCC	Integrated gasification combined-cycle	
IPPC	Integrated Pollution Prevention and Control	
IPTS	Institute for Prospective Technological Studies	
K	Kelvin	
kPa	Kilo Pascal	
kV	Kilo Volt	
kWel	Kilowatt electric	
LDAR	Leak detection and repair programme	
LEA	Low excess air combustion	
LFO	Light Fuel Oil	
LICADO	Liquid Carbon Dioxide	
LIMB	Limestone Injection Multistage Burner	
<u>LNB</u> LPG	Low NOx Burners Liquefied petroleum gas	
LRK		
	Long rotary kiln	
mg/l mg/m <sup>3</sup>	Milligramme per litre Milligramme per cubic metre	
mg/m mg/Nm <sup>3</sup>		
	Milligramme per normal cubic metre	
mg/t	Milligramme per ton	Mis en forme : Français (France)
MCR	Maximum Continuous Rating	
MFSK	Mixed feed shat kiln	
Mg	Megagramme, metric ton	

Ni	Nickel
Mn	Manganese
Mo	Molybdenum
MSW	Municipal solid waste
MW	Mega Watt
MWth	Mega Watt Thermal
MWe	Mega Watt Electric
µg/Nm <sup>3</sup>	Microgramme per normal cubic metre
μm	Micrometer
<u>N</u> <sub>2</sub>	Nitrogen
NaHCO <sub>3</sub>	Sodium bicarbonate
NO <sub>x</sub>	Nitrogen oxide
NFM	Non ferrous metal
NMVOC	Non-methane volatile organic compounds
<u>O</u> <sub>2</sub>	Oxygen
00	Organic Carbon
OFA	Over Fire Air
OSK	Other shaft kiln
PAH	Polycyclic aromatic hydrocarbon
PCDD/F	polychlorinated dibenzodioxin/furan
PCDF	Polychlorinated dibenzofurans
PFBC	Pressurized fluidized bed combustion
PFRK	Parallel flow regenerative kiln
PM	Particulate matter
PM <sub>2,5</sub>	Particulate matter (2,5 micrometer)
PM <sub>10</sub>	Particulate matter (10 micrometer)
ppm	Parts per million
PRK	Pre-heater rotary kiln
RAINS	Regional Air Pollution Information and Simulation
RAP	Reduced air preheat
SCR	Selective Catalytic Reduction
SG	Spark Gas (engines)
SNCR	Selective non-catalytic reduction
SRA	Sulphur Reducing Additives
SRU	Sulphur Recovery Unit
SO <sub>2</sub>	Sulphur dioxide
TA-LUFT	Technische Anleitung zur Reinhaltung der Luft (Technical Instructions on Air
	Quality Control)
TCC	Thermal catalytic cracking
TOC	Total organic carbon
<u>TSP</u>	Total Suspended Particles
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Programme
VOC	Volatile Organic Compound
WMO	World Meteorological Organisation

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## Acronyms used

The following a	cronyms are used throughout the guidance document:	
BAT	Best available technique	Mis en forme : Taquets de
BC	Black carbon	tabulation : Pas à 1.5 cm + 4 cm
BREF	Best available technique reference document	
	Used in the same way as TSP	
ELV	Emission limit value	
ESP	Electrostatic precipitator	
FF	Fabric Filter	
FGD	Flue gas desulphurisation	
IGCC	Integrated gasification combined-cycle	
	Cubic meter at standard conditions (101,325 kPa and 273.15 K)	
	Total Suspended Particles	
SCR	Selective Catalytic Reduction	
SNCR	Selective Non-Catalytic Reduction	
	In the context of the Gothenburg Protocol, all organic compounds of an nature, other than methane, that are capable of producing photochemical oxidant by trogen oxides in the presence of sunlight	Mis en forme : Retrait : Gauche : 0 cm, Espace Avant : 3 pt, Taquets de tabulation : Pas à 1.5 cm + 14.75 cm

## 1 Introduction

The aim of this document is to provide the Parties to the Convention on Long-Range Transboundary Air Pollution with guidance on identifying best abatement options, with particular reference to best available techniques (BAT) to enable them to meet the obligations of the Protocol to abate Acidification, Eutrophication, Ground Level Ozone and dust (including  $PM_{10}$ ,  $PM_{2,5}$  and BC).

This guidance document addresses lists control options for the following pollutants:

- the control options for NO<sub>x</sub> emissions defined as the sum of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) expressed as nitrogen dioxide (NO<sub>2</sub>).
- the control options of sulphur emissions considered including as all sulphur compounds expressed as sulphur dioxide (SO<sub>2</sub>).
- the control options of VOC emissions considered defined as all organic compounds of an anthropogenic nature, other than methane, that are capable of producing photochemical oxidant by reaction with nitrogen oxides in the presence of sunlight.
- the control options of particulate matter (PM) emissions consisting of a mixture of particles suspended in the air including dust or Total Suspended Particulate Matter (TSP), (including PM<sub>10</sub>, PM<sub>2.5</sub> and black carbon (BC)) whose definitions are as follows:
- $PM_{2.5}$ ; particles with an aerodynamic diameter equal to or less than 2.5 microns ( $\mu$ m);
- PM<sub>10</sub>: particles with an aerodynamic diameter equal to or less than 10 microns (µm);
- Dust<u>dust or TSP</u>: for the purpose of the guidance document "dust" and "total suspended particulate matter" (TSP) means the mass of particles, of any shape, structure or density, dispersed in the gas phase at the sampling point conditions which may be collected by filtration under specified conditions after representative sampling of the gas to be analyzed, and which remain upstream of the filter and on the filter after drying under specified conditions.
- black carbon (BC): carbonaceous particulate matter that absorbs light.

In the context of this guidance document, dust and TSP have the same meaning. As can be seen from chapter 6, abatement techniques for dust in general also provide high removal efficiency for PM<sub>10</sub>, and in some cases, PM<sub>2.5</sub>. However, some measures will reduce coarse particles much more efficiently than finer particles such as PM<sub>2.5</sub>; therefore, specific measures targeting PM<sub>2.5</sub> and BC are necessary.

As monitoring data for specific fractions of particulate matter such as  $PM_{2.5}$  and  $PM_{10}$  are in general not presently available, emission levels are defined for dust.

The expression "Best available techniques" means the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to prevent and, where that is not practicable, to reduce emissions and the impact on the environment as a whole:

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

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

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

Criteria for determining BAT are as follows:

- 1. the use of low-waste technology;
- 2. the use of less hazardous substances;
- 3. the furthering of recovery and recycling of substances generated and used in the process and of waste, where appropriate;

4. comparable processes, facilities or methods of operation which have been tried with success on an industrial scale;

5. technological advances and changes in scientific knowledge and understanding;

6. the nature, effects and volume of the emissions concerned;

7. the commissioning dates for new or existing installations;

8. the length of time needed to introduce the best available technique;

9. the consumption and nature of raw materials (including water) used in the process and energy efficiency;

10. the need to prevent or reduce to a minimum the overall impact of the emissions on

the environment and the risks to it;

11. the need to prevent accidents and to minimize the consequences for the environment;

12. information published by national and international organisations.

This guidance document presents BAT Associated Emission Levels (AELs) which can be described as follows:

- BAT AELs are levels that an operator can expect to achieve when using the BAT, and are appropriate reference points to assist in the determination of permit conditions,
- BAT AELs represent average emission levels achievable during a substantial period of time in normal operating and/or design conditions (well-proven technology),
- BAT AELs are neither emission nor consumption limit values.

BAT AELs are based on normal operating conditions and may vary with changing input materials or for varying outputs.

The BATAELs are based on a range of averaging periods and represent a typical load situation. Therefore, when taking account of BATAELs in the context of ELV setting, proper regard must always be given to the reference period to which the described BATAEL pertains. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

Where a level is described as "achievable" using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

Unless otherwise indicated, the reduction measures listed are considered, on the basis of operational experience of several years in most cases, to be the most well-established and economically feasible best available techniques. BAT Associated Emission Levels are generally expressed in mg/m<sup>3</sup> (dry gas, 273.15K and 101.325 kPa except is stipulated different) as daily average. For organic solvent uses they can be expressed in % of solvents used (solvents purchased + solvents internally recycled). The continuously expanding experience with low-emission measures and technologies at new plants as well as with the retrofitting of existing plants will necessitate regular review of this document.

Although this guidance document lists a number of measures and technologies, spanning a wide range of costs and efficiencies, it cannot be considered as an exhaustive statement of control options. Moreover, the choice of control measures and technologies for any particular case will depend on a number of factors, including current legislation and regulatory provisions and, in particular, control technology requirements, primary energy patterns, industrial infrastructure, economic circumstances and specific in-plant conditions.

This guidance document provides options and techniques, along with their performance assessment for emission prevention and reduction of Sulphur,  $NO_x$ , VOCs, dust (including  $PM_{10}$ ,  $PM_{2,5}$  and BC). However, the reduction of a given pollutant cannot be considered without taking into account the risk of generating other pollutants and/or increasing energy consumption. It is worthwhile to consider them together along with such other pollutant-specific control options in order to maximize the abatement

effect and minimize the impact on the environment. Respective co-benefit/trade-off between different pollutants have to be carefully accounted for. This is particularly important for multi-pollutant/multi-effect approach where positive/negative effects on the reduction of Greenhouse Gases (GHGs) are possible (For example, measures that improve the efficiency of combustion will generally reduce both BC and  $CO_2$ ).

This guidance document provides options and techniques, along with their performance assessment for emission prevention and reduction of Sulphur,  $NO_x$ , VOCs, dust (including  $PM_{10}$ ,  $PM_{2,5}$  and BC). Performance and costs are documented in a series of documents elaborated by EGTEI, in the draft background document submitted to the UNECE Task Force on Heavy Metals (TFHM) of 2006, the EU Commission with the different Best Available Reference documents (BREF) and other recent publications, US EPA reports and a series of documents acknowledged nationally or internationally.

In this document, both primary and secondary measures are considered. Primary reduction measures aim at reducing pollutant emissions at their sources of formation. Secondary measures aim at treating waste gases containing already formed pollutants (add-on or end of pipe technologies).

This guidance document covers the stationary sources emitting Sulphur, NOx, VOCs, dust (including  $PM_{10}$ ,  $PM_{2,5}$  and BC)\_listed in table 1. Mobile sources (road traffic, non road traffic –and off road machineries) are covered by the guidance document on mobile sources. Some stationary sources are not covered by this guidance document but may be significant sources of BC for some countries, such as agricultural burning, open biomass burning, flares in gas and petroleum extraction, <u>existing stationary diesel engines</u>.

Table 1: stationary sources for emissions of sulphur, NOx, VOCs, dust (including PM <sub>10</sub> , PM <sub>2.5</sub>
and BC) covered by this guidance document

		SO <sub>2</sub>	NOx	Dust	BC	VOCs
7-1	Combustion installation < 1MW with domestic combustion installation included	Y	Y	Y	Y	Y
7-2	Combustion installations from 1 to 50 MW	Y	Y	Y	V	Y
	(a) Boilers (b) Gas turbines	Ŷ	Ŷ	ř	Y	ř
7-3	Combustion installations > 50 MW	Y	Y	Y	Y	Y
	(a) Boilers (b) Gas turbines	I	T	T	I	T
7-4	Mineral oil and gas refineries					
	Combustion and furnaces for emissions of SO <sub>2</sub> , NOx and dust (including $PM_{10}$ , $PM_{2,5}$ and BC) including processes heaters, FCC, TCC and flares)	Y	Y	Y	Y	
7-5	Mineral oil and gas refineries					Y
	Processes and sources of NMVOC					ř
7-6	Coke oven furnaces	Y	Y	Y	Y	Y
7-7	Iron and steel production (iron and steel making in integrated steelworks (sinter plants, pelletization plants, blast furnaces and basic oxygen furnaces including continuous and ingot casting) and electric arc furnace steelmaking)	Y	Y	Y	Y	Y
7-8	Ferrous metals processing					
	iron foundries with a capacity exceeding 20 tonnes/day, as well as installations for "hot and cold forming", including hot rolling, cold rolling, wire drawing, installations for "continuous coating", including hot dip coating and coating of wire, and installations for "batch galvanizing"	Y	Y	Y	Y	Y
7-9	Non ferrous metal processing industry (primary and secondary Al production, primary and secondary Pb production, primary and secondary Zn production and primary and secondary Cu production)	Y	Y	Y	Y	
7-10	Cement production	Y	Y	Y	Y	
7-11	Lime production	Y	Y	Y	Y	
7-12	Glass production	Y	Y	Y	Y	
7-13	Man-made fibre production	Y	Y	Y	Y	Y
7-14	Ceramics manufacturing industry	Y	Y	Y	Y	
7-15	Paper pulp production	Y	Y	Y	Y	
7-16	Nitric acid production	Y	Y	Y		
7-17	Sulphuric acid production	Y	Y	Y		
7-18	Waste incineration (domestic and industrial waste, waste water treatment sludge incineration)	Y	Y	Y	Y	
7-19	Industrial wood processing			Y		
7-20	Petrol distribution – from the mineral oil refinery dispatch stations (petrol) to service stations including transport and depots (petrol)					Y
7-21	Storage and handling of organic compounds (except petrol covered by chapters 7.5 and 7.21)					Y

Table 1: stationary sources for emissions of sulphur, NOx, VOCs, dust (including PM <sub>10</sub> , PM <sub>2.5</sub>
and BC) covered by this guidance document

		SO <sub>2</sub>	NOx	Dust	BC	VOCs
7-22	Production of organic chemicals (excluding fine organic chemical production)					Y
7-23	Production of organic fine chemicals					Y
7-24	Adhesive coating (including footwear manufacture)					Y
	General coating, shoe industry, lamination					Ť
7-25	Coating processes 1					
	Manufacture of cars					Y
	Manufacture of truck cabins, trucks					Ť
	Manufacture of buses and trailers					
7-26	Coating processes 2					Y
	Winding wire coating					Ŷ
7-27	Coating processes 3					V
	Coil coating					Y
7-28	Other coating processes 4					X
	Other industrial coating					Y
7-29	Solvent content in products 1: Domestic and architectural paints					Y
7-30	Manufacturing of coatings, varnishes, inks and adhesives					Y
7-31	Printing processes (Packaging printing, cold set offset					
	heat set offset, publication sector, screen printing)					Y
7-32	Rubber processing					Y
7-33	Dry cleaning					Y
7-34	Metal degreasing					Y
7-35	Vegetable oil and animal fat extraction and vegetable oil refining					Y
7-36	Vehicle refinishing					Y
7-37	Wood impregnation					Y
7-38	Solvent content in products 2:					
	Domestic uses of solvent (other than paints)					Y
7-39	Beer production					Y
7-40	Titanium dioxide production	Y	Y	Y		
7-41	New stationary gas and diesel engines		Y	Y	Y	

## Acronyms used

The following a	acronyms are used throughout the guidance document:	
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BC	Black carbon	tabulation : Pas à 1.5 cm + 4 cm
BREF	Best available technique reference document	
	Used in the same way as TSP	
ELV	Emission limit value	
ESP	Electrostatic precipitator	
FF	-Fabric Filter	
FGD	Flue gas desulphurisation	
IGCC	Integrated gasification combined-cycle	
	<sup>—</sup> Cubic meter at standard conditions (101,325 kPa and 273.15 K)	
TSP	Total Suspended Particles	
	Selective Catalytic Reduction	
	Selective Non-Catalytic Reduction	
	In the context of the Gothenburg Protocol, all organic compounds of an anthropogenic <sup>4</sup> than methane, that are capable of producing photochemical oxidant by reaction with the presence of sunlight	<b>Mis en forme :</b> Retrait : Gauche : 0 cm, Première ligne : 0 cm, Taquets de tabulation : Pas à 1.5 cm + 4 cm

# 2 Common general issues for <u>all</u> the pollutants considered<u>in this</u> report

#### 2.1 Monitoring and reporting

Several monitoring systems, using both continuous and discontinuous measurement methods, are available. However, quality requirements vary. Measurements are to be carried out by qualified institutes using measuring and monitoring systems that meet international standards. To this end, a certification system can provide the best assurance.

In the framework of modern automated monitoring systems and process control equipment, reporting does not create a problem. The collection of data for further use is a state-of-the-art technique. However, data to be reported to competent authorities differ from case to case. To obtain better comparability, data sets and prescribing regulations should be harmonized. Harmonization is also desirable for quality assurance of measuring and monitoring systems. This should be taken into account when comparing data.

To prevent discrepancies and inconsistencies, key issues and parameters, including the following, must be well defined:

- definition of standards expressed as ppmv, mg/Nm<sup>3</sup>, g/GJ, kg/h or kg/Mg of product. Most of these units need to be calculated and need specification in terms of gas temperature, humidity, pressure, oxygen content or heat input value;
- (b) definition of the period over which standards are to be averaged, expressed as hours, months or a year, and of the measuring method;
- definition of failure times and corresponding emergency regulations regarding bypass of monitoring systems or shutdown of the installation;
- (d) definition of methods for backfilling data missed or lost as a result of equipment failure;
- (e) definition of the parameter set to be measured. Depending on the type of industrial process, the necessary information may differ. This also involves the location of the measurement point within the system.

Quality control of measurements has to be ensured.

#### 2.2 Energy management, energy efficiency, energy mix

The major part of the sulphur, NOx, and dust (including  $PM_{10}$ ,  $PM_{2,5}$  and BC) emissions from stationary installations result from fuel combustion to produce heat and power. Reducing fuel combustion via an efficient and rational use of energy (energy management) may be therefore an efficient measure to reduce these air emissions but also the emissions of other pollutants and of greenhouse gases. Energy management may also contribute to increasing security of energy supply and a reduced consumption of natural resources. On the level of stationary installations but also on the level of production sites energy management means to increase overall energy efficiency by a number of different measures which can be realized alone or at best in combination like:

- implementation of an energy efficiency management system (ENEMS)
- establishment of a systems view for energy efficiency
- benchmarking
- energy efficient design (EED)
- process integration
- expertise and know-how gains on energy efficiency
- effective control, maintenance and monitoring of installations

BAT is the optimisation of the combustion and steam systems but also the systems for compressed air, pumping, heating, cooling, ventilation, lighting, and other physical and chemical processes using a

large number of techniques. Of particular importance are also heat recovery and cogeneration if reasonable [from [1]].

Besides energy management which focuses more on the demand side, the supply side for energy has also a large impact on air emissions. Besides fuel switch where one (fossil) fuel is replaced by another also a change in the energy mix should be considered taking into account country specific conditions such as infrastructure, energy policy and availability of resources of fossil fuels and renewable energy like wind power, solar energy, geothermal energy or biomass. Burning more biomass, especially in stoves, may, however, also lead to increasing air emissions.

Reference used for this chapter:

[1] European Commission (2008): Reference Document on Best Available Techniques, Energy Efficiency]

# 3 General issues for sulphur

#### 3.1 General issues

In order to reduce SOx emissions from combustion processes or other sources, different types of measures are applied. The main applied techniques: energy efficiency improvement, fuel switching, fuel cleaning, primary and secondary measures are presented in this chapter.

 $SO_2$  is a major contributor to acidification, via the formation in the atmosphere, of sulphate and sulphuric acid.  $SO_2$  residence time in atmosphere depends on meteorological conditions. The average residence time is about 3 to 5 days, hence  $SO_2$  can be transported over hundred kilometres.

To achieve the most efficient SOx emission reduction, beyond energy management measures, a combination of measures should be considered.

# 3.2 Sulphur content of fuels

Sulphur present in fuels reacts with oxygen contained in combustion air to form  $SO_2$ . Therefore  $SO_2$  emissions arising from combustion are directly related to the sulphur content of fuels used.  $SO_3$  is produced by oxidation of  $SO_2$ , during combustion.

Sulphur content of solid fossil fuels ranges from 0.5 % to more than 5 %. Solid fossil fuels are the largest sources of  $SO_2$  [1]. Sulphur content of natural gas is very low as well as sulphur content of wood. Sulphur content of liquid fossil fuels ranges from 0.001 % to more than 5 %. The availability of low sulphur content liquid fossil fuels requires the removal of sulphur at the refinery and the adoption of specific processes.

During the last decade, national and European legislation have toughened the limits required for the sulphur content of petroleum products. The table 2 presents the typical limit values applied for liquid fuels in the EU [2].

#### Table 2: typical limit values applied for liquid fuels in the EU

Fuel	Current sulphur content (% weight)	EU directive
Residual oil	< 1 % or 10000 ppm	1999/32/EC
Gas-oil	< 0.1 % or 1000 ppm	1999/32/EC

#### 3.3 Fuel switching

Fuel switching (e.g. from high- to low-sulphur coals and/or liquid fuels, or from coal or liquid fuel to gas) leads to lower sulphur emissions, but there may be certain restrictions, such as the availability of low-sulphur fuels and the adaptability of existing combustion systems to different fuels. In many EU countries, some coal or oil combustion plant is being replaced by gas-fired combustion plant. Dual-fuel plant may facilitate fuel switching. Fuel switching can also have beneficial effects on nitrogen dioxide or particulate matter emission levels.

#### 3.4 Fuel cleaning

Cleaning of natural gas is state-of-the-art technology and widely applied for operational reasons. Cleaning of process gas (acid refinery gas, coke oven gas, biogas, etc.) is also state-of-the-art technology. Desulphurization of liquid fuels (light and medium fractions) is state-of-the-art technology. Desulphurization of heavy fractions is technically feasible; nevertheless, the crude oil properties should be kept in mind. Desulphurization of atmospheric residue (bottom products from atmospheric crude distillation units) for the production of low-sulphur fuel oil is not, however, commonly practised; processing low-sulphur crude is usually preferable. Hydro-cracking and full conversion technology has matured and combine high sulphur retention with improved yield of light products. The number of full conversion refineries is constantly rising. Such refineries typically recover 80 to 90% of the sulphur intake and convert all residues into light products or other marketable products. This type of refinery

consumes more energy and requires higher investments. Sulphur content of refinery products needs to correspond to the restricted value ordered by the EU and provided in table 2. Current technologies to clean hard coal can remove approximately 50% of the inorganic sulphur (depending on coal properties) but none of the organic sulphur. More effective technologies are being developed. However, they require higher specific investments. Thus the efficiency of sulphur removal by coal cleaning is limited compared to flue gas desulphurisation. There may be a country-specific optimisation potential for the best combination of fuel cleaning and flue gas cleaning.

## 3.5 Combustion Technologies

Advanced combustion technologies may improve thermal efficiency and reduce sulphur emissions. These technologies include fluidized-bed combustion (FBC), integrated gasification combined-cycle (IGCC); and combined-cycle gas turbines (CCGT). Stationary combustion turbines can be integrated into combustion systems in existing conventional power plant. This can increase overall efficiency by 5 to 7%, leading, for example, to a significant reduction in SO<sub>2</sub> emissions. However, major alterations to the existing furnace system become necessary. Reciprocating engines can also increase the electrical efficiency by taking advantage of the sensible heat of the exhaust gases generated by e.g. use of a feed-water combined cycle.

In FBC, the combustion takes place through a particulate bed, which can be fixed (FFBC), pressurized (PFBC), circulating (CFBC) or bubbling (BFBC). Fluidized-bed combustion is a combustion technology for burning hard coal and brown coal, but it can also burn other solid fuels, such as petroleum coke, and low-grade fuels, such as waste, peat and wood. Emissions can be further reduced by integrated combustion control in the system due to the addition of lime/limestone to the bed material. The use and/or disposal of by-products from this process may cause problems and further development is required.

The IGCC process includes coal gasification and combined-cycle power generation in a gas and steam turbine. The gasified coal is burnt in the combustion chamber of the gas turbine. Sulphur emission control is achieved by using state-of-the-art technology for raw gas cleaning facilities upstream of the gas turbine. The technology also exists for heavy oil residues and bitumen emulsions.

Combustion modifications comparable to the measures used for NOx emission control do not exist, as during combustion the organically and/or inorganically bound sulphur is almost completely oxidized. A certain percentage, depending on the fuel properties and combustion technology, is retained in the ash. The amount of sulphur retained in ash, can be influenced by added sorbents (e.g. lime/limestone) and combustion conditions (e.g. temperature). In this guidance document dry additive processes for conventional boilers are considered as process modifications due to the injection of an agent into the combustion unit. However, experience has shown that, when applying these processes, thermal capacity is lowered, and the Ca/S ratio is relatively high and sulphur removal low. In recent years, the performance of these processes has nevertheless been optimized to the point that SO<sub>2</sub> removal efficiency reached 50 - 80%. Problems with the further use of the by-product have to be considered.

#### 3.6 Secondary measures - Flue gas desulphurisation processes

These processes aim at removing already formed sulphur oxides, and are considered as secondary measures. Sulphur removal using wet, dry or semi-dry processes are used to treat the flue gases. Sulphur can also be removed using the recovery of sulphur dioxide from the flue gases. It is then either extracted (regenerative process) or converted into sulphuric acid (sulphuric acid plant). Flue gas scrubbing using water or seawater is another available technology to reduce  $SO_2$  emissions.

In wet scrubbing technologies, the flue gas is first dedusted then cleaned by an atomized solution of alkaline compounds.  $SO_2$  reacts with these alkaline compounds to form by products, whose chemical nature depends on the alkaline compound used. In the case of use  $CaCO_3$  or CaO, by products may be upgraded as gypsum if some technical conditions are achieved. By products can also be upgraded using other scrubbing agent. With wet FGD, excellent efficiencies can be achieved ranging from 92 to 98% with a near-stoichiometry Ca/S ratio. This process is mainly used for reducing  $SO_2$  emissions from coal power plants.

In the dry process, a calcium or sodium based sorbent is injected in solid form into the flue gases before a fabric filter or an ESP. Hydrated lime  $(Ca(OH)_2)$  or sodium bicarbonate  $(NaHCO_3)$  are the most frequently used sorbents. Sorbents need to be very reactive and are activated for this purpose (finely ground  $CA(OH)_2$  with high activity as example). They react with SO<sub>2</sub> to form calcium or sodium sulphites and sulphates, which need then to be filtered in order to reduce dust emissions. The dry duct injection process efficiency is lower than with wet FGD (about 50 %–)\_and depends on several parameters such as temperature, SO<sub>2</sub> content of the flue gas, Ca/S ratio and residence time.

Furnace sorbent injection is a direct injection of a dry sorbent in the gas stream of the boiler furnace. Pulverised limestone is used ( $CaCO_3$ ). Calcium sulphites and sulphates formed need to be captured by FF or ESP. Efficiencies from 70 to 80 % may be obtained according to the arrangement used [4].

The semi-dry process or spray dry scrubbing is similar to the dry process and also produces a solid residue. It uses moisturised lime or limestone containing about 10% of water to enhance the contact and the reactions. The removal  $SO_2$  efficiency ranges from 85 to 92% with a ratio Ca/S from 1.3 to 2 [4].

In regenerative processes, a regenerating agent is used to recover  $SO_2$ . The sodium sulphite bisulphite process is one of these regenerative processes. Sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>) reacts with SO<sub>2</sub> to form sodium bisulphite (NaHSO<sub>3</sub>), which is then evaporated to crystallise sodium sulphite and recover SO<sub>2</sub>. A recovery rate of more than 95% can be achieved. This type of process is commonly used in titanium dioxide production plants. This process requires qualified operating staff.

In sulphuric acid production, SO<sub>2</sub> is first oxidised to SO<sub>3</sub> which is absorbed to form sulphuric acid. The sulphuric acid production process can include a single absorption stage or a double one depending on the conversion rate to be achieved. Double absorption sulphuric acid plant is more effective.

Flue gas desulphurisation is a high capital cost process best suited to high load factor plant.

The following table presents general results for several flue gas desulphurisation processes.

# Table 3: general description and performance for selected flue gas desulphurisation processes [3]

	Wet scrubbing	Dry scrubbing	Regenerative process	Acid sulphuric plant (double absorption)
Efficiency	Desulphurisation rate of 95 % to 98%) for a Ca/S ratio from 1.02 to 1.1	Desulphurisation rate of 50 % to 80% depending on the Ca/S ratio and systems (dry duct injection or furnace injection)	Recovery rate of 95-98 %	Conversion rate of > 99%
By-product	Gypsum can be obtained under certain conditions and can be suitable for use in plasterboard production	Calcium sulphite and sulphate not recoverable		
Limits	Possible problem of scaling	Not cost effective, large amount of waste to be treated accordingly		Inlet dust concentration < 30 mg/Nm <sup>3</sup> Inlet $O_2$ concentrations to be 5 times higher than SO <sub>2</sub> concentrations.

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To achieve the most efficient process for sulphur emission reductions beyond the energy management measures listed above, a combination of technological options identified in the paragraphs above should be considered. In some cases, options for reducing sulphur emissions may also reduce emissions of  $NO_x$  and other pollutants.

# 3.7 Costs of reduction techniques of SO<sub>2</sub>

Costs are an important issue when selecting  $SO_2$  emission reduction techniques. The following expenses may be relevant:

- imputed depreciation allowance and imputed interest,
- labour costs,
- expenses for auxiliary and operating materials,
- energy costs,
- maintenance and repair costs, expenditure on monitoring, expenses for external services,
- taxes, environmental levies (e.g. charges for waste water), fees, public charges.

Costs increase in general less than the capacity of the reduction technique so that larger units are often more cost-effective or unit with higher flue gas sulphur content. Dry additive processes are less cost effective for high sulphur content fuels compared to wet scrubbing processes.

Costs of SO<sub>2</sub> abatement techniques are developed in chapter 7.

# 3.8 By products and side effects

Side effects of emission abatement options/techniques can be positive or negative and should be accounted for.

Options that lead to usable by-products should be selected, as should options that lead to increased thermal efficiency and reduced waste whenever possible. Although most by-products such as gypsum, ammonia salts, sulphuric acid or sulphur, are usable or recyclable products, factors such as market conditions and quality standards need to be taken into account.

Side effects can generally be limited by properly designing and operating the facilities. Side effects include

- impacts on energy consumption and hence greenhouse gas emissions,
- impacts on other air pollutants,
- impacts on the use of natural resources such as limestone,
- cross-media effects, e.g. on waste or water.

More particularly, the following table presents positive and negative side effects for selected flue gas desulphurisation processes.

#### Table 4: positive and negative side effects for selected flue gas desulphurisation processes

Abatement technique	Positive side effect	Negative side effect
Dry scrubbers or additive injection process	Reduction of dust and heavy metals	Calcium sulphite and sulphate not recoverable
		Large amount of waste produced
Wet scrubbers	Reduction of dust and heavy metals Possible upgrade of by-products to gypsum	Water consumption
		Energy consumption
		Limestone consumption
		Waste generation

#### 3.9 References used in chapter 3

[1] DGEMP, direction générale de l'énergie et des matières premières,

http://www.industrie.gouv.fr/energie/,

[2] European directive 1999/32/ EC, UEOJ 26<sup>th</sup> April 1999.

[3] Techniques de désulphurisation des procédés industriels, ADEME, 1999.

[4] LCP BREF (2006): Reference Document on Best Available Techniques for Large Combustion Plants. – European Commission, 618 pp.

# 4 General issues for NOx

#### 4.1 General issues

The generic term NOx refers to the sum of nitrogen oxide (NO) and nitrogen dioxide (NO<sub>2</sub>), expressed as NO<sub>2</sub>. Nitrous oxide (N<sub>2</sub>O), a greenhouse gas, is not covered in NOx. The main source for NOx is combustion where primarily NO is formed [1]. NO is then rapidly converted to NO<sub>2</sub>.

NOx emissions contribute to acidification via formation of nitrous acid ( $HNO_2$ ) and nitric acid ( $HNO_3$ ), to eutrophication, to tropospheric ozone formation and (in particular  $NO_2$ ) to irritation and damage to respiratory organs. Furthermore, NOx may react with ammonia to form secondary fine particles with negative health effects.

In combustion, three main types of NOx formation are distinguished:

- thermal NOx: molecular nitrogen (N<sub>2</sub>) from air and molecular oxygen (O<sub>2</sub>) dissociate at high temperature and react to form NOx. The reaction is reversible and usually becomes significant at temperatures above around 1300 °C [1]. NOx formation increases with temperature and residence time.
- fuel NOx: in fuel NOx, the nitrogen source for NOx formation is the fuel itself. Two path ways
  may be distinguished: i) during initial combustion, volatiles including oxidized nitrogen are
  released and ii) during later stages when the char is oxidized and the nitrogen contained in the
  char is oxidized to NOx. Fuel NOx formation is significant at temperatures above about 800°C.
  The amount of fuel NOx depends on the N content of fuels and on combustion conditions.
- prompt NOx: fuel radicals react with molecular nitrogen (N<sub>2</sub>) from the air to form NOx. Compared to thermal and fuel NOx, prompt NOx is of lesser importance for the sources considered here.

In order to reduce NOx formation and NOx emissions from combustion processes different types of measures like energy efficiency improvements (cf. Chapter 2), fuel switch as well as primary and secondary measures are applied. To achieve the most efficient NOx reduction, beyond energy management measures, a combination of measures should be considered. To identify the best combination of measures, a site-specific evaluation is needed.

#### 4.2 Fuel switching

Switching to low NOx producing fuels is one option to reduce NOx emissions but is governed by country specific conditions such as infrastructure and energy policy. Fuels with high nitrogen content like heavy fuel oil and coal may lead to high fuel NOx formation and hydrogen rich fuels like natural gas as a result of high combustion temperatures to high thermal NOx formation. The choice of the fuel may also have effects on other emissions like sulphur, particulate matter and greenhouse gas emissions as well as on applicability and need of abatement measures.

#### 4.3 Fuel cleaning

Fuel cleaning to remove nitrogen is not a commercial option. Hydroprocessing in refineries, however, also reduces the nitrogen content of end products.

#### 4.4 Primary measures

Primary measures reduce NOx generation at the source by a number of different principles or methods or a combination of them [1]:

- reducing peak temperature,
- reducing residence time at peak temperature,
- chemical reduction of NOx during combustion process,
- reducing nitrogen in the combustion process.

In the following paragraphs, an overview on available primary measures is given. Their applicability depends on the industrial sector and the production process.

**Reducing peak temperature**: As thermal NOx formation depends largely on the combustion temperature, a reduction in temperature is one option to reduce NOx formation. Reducing peak temperature can be achieved by the following methods i) diluting the heat produced during the combustion process, ii) cooling down, and iii) reducing the oxygen available for combustion [1] but also by applying other combustion techniques like fluidized bed combustion (FBC) which operates at lower temperatures and includes an inherent air-staging. Main methods for reducing peak temperature are:

- substoichiometric combustion, i.e. using a fuel-rich mixture so that oxygen is a limiting factor (fuel acts also as reducing agent),
- suprastoichiometric combustion, i.e. using a fuel-lean mixture to dilute combustion heat,
- injecting cooled oxygen-depleted fuel gas to dilute combustion heat,
- injecting cooled oxygen-depleted fuel gas with added fuel to dilute combustion heat, to reduce the reaction temperature and to make oxygen a limiting factor,
- injecting water or steam to dilute combustion heat and to reduce the reaction temperature.

**Reducing residence time at peak temperature**: As thermal NOx formation depends largely on the time the fuel gas remains in the high temperature region, reducing this residence time reduces also NOx formation. Methods to reduce residence time include [1]:

- injection of fuel, steam, re-circulated flue gas or combustion air immediately after combustion,
- reducing the extension of the high temperature zone which can be faster left by the flue gas then.

**Chemical reduction of NOx during combustion process**: NOx can be reduced to  $N_2$  using a reducing agent which is itself oxidized. The principle of chemical reduction is widely used in secondary measures but can be also used as a primary measure when reduction takes already place during the combustion process. Main methods are:

- substoichiometric combustion, i.e. in a fuel rich mixture so that the remaining fuel may act as reducing agent,
- re-burning of the flue gas with fuel added (with the added fuel acting as a reducing agent),
- generation of fuel-lean and fuel-rich conditions in the combustion zone.

**Reducing nitrogen in the combustion process**: Reducing NOx formation by reducing the available nitrogen can be achieved using nitrogen poor fuels like natural gas (see fuel switch) as well as by using oxygen instead of air for the combustion process.

The following primary measures which are based on the principles and methods described above are mainly in use, each with its specific advantages and disadvantages, cf. e.g [1], [11]. Some of the primary measures are typical for retrofit, others for new installations and others are only applicable in new installations.

- **Iow excess air combustion (LEA):** In order to ensure complete combustion air is often added in large excess which may result in higher thermal NOx formation when air nitrogen is oxidized [2], [3], [4]. Reducing the excess air reduces also NOx formation.
- flue gas recirculation (FGR): Re-circulating cooled flue gas reduces the combustion temperature in a secondary combustion stage and also oxygen concentration so that thermal NOx formation is reduced. Heat of the flue gas may be recovered in a heat exchanger [1], [5].
- air staging (AS): The principle of air staging is to create two zones, one fuel-rich zone where initial combustion takes place and a second one where air is added to ensure complete combustion. This allows reducing thermal NOx formation in the first zone where less nitrogen is available and in the second where temperature is lower. The zone may be created in different ways. In Biased Burner Firing (BBF) air and fuel flow rates are varied, in Burners Out of Service (BOOS) the fuel flow to the burner is cut for a short time and in Overfire Air (OFA) air

is injected above the normal combustion zone [3], [4], [5]. Staged air combustion is frequently used in conjunction with Low NOx burners (LNB).

- **fuel staging (FS):** Fuel staging is similar to air staging but with fuel instead of air. The first stage is extremely fuel-lean which reduces the temperature. Fuel added in the second stage acts as a reducing agent for formed NOx. In a third stage air is added to ensure burnout [6].
- **fuel re-burning (FR)**: Fuel re-burning is similar to flue gas recirculation (FGR) but with added fuel in the flue gas leading to lower temperatures. If added in a second combustion stage fuel re-burning makes use of the fuel as reducing agent and is similar to fuel staging (FS).
- **reduced air preheat (RAP)**: Combustion air is in general preheated by the flue gases to cool them down in order to improve efficiency. Reducing this preheating reduces also flame temperature and hence NOx formation but also overall energy efficiency [1], [3].
- Iow NOx burners (LNB): Low NOx burners mix fuel and air/flue gas in a way so that different zones are created as in staged combustion. The zoning allows lower flame temperature and oxygen concentration as well as chemical reduction of NOx by fuel in some of the zones [1], [5]. Low NOx burners can be further differentiated into air-staged LNB, flue-gas recirculation LNB and fuel-staged LNB depending on the principle used for reducing NOx emissions. A further development is the Ultra low NOx burner.
- water/steam injection: Water and steam are injected to cool the flame and to reduce thermal NOx formation.
- oxycombustion: In oxycombustion the combustion air is replaced by oxygen so that no thermal NOx is produced. So far oxycombustion is to a larger extent only applied for glass production but its use might become more emerging in future as oxycombustion is one option to achieve high CO<sub>2</sub> concentrations in flue gas which is an advantage for CO<sub>2</sub> capture and sequestration [7].
- **combustion optimisation**: In combustion optimisation the combustion process is actively controlled, e.g. by making use of specialised software. One option is to slightly decrease combustion efficiency in order to reduce NOx emissions [1].
- **catalytic combustion**: Using a catalyst to reduce combustion temperature below NOx formation temperature may reduce NOx emissions very strongly. However, applications are still rare in practice [1] though gas turbines seem to be an interesting field of application [8].

The techniques reported in § 4.4 are an inventory of available technologies to reduce NOx emissions, which does not mean that those reported technologies are applicable to each industrial sector or process of production.

For new stationary gas and diesel engine measures, refer to document 7-41.

#### 4.5 Secondary measures

Secondary measures (add-on or end of pipe technologies) reduce the emissions of already formed NOx to the environment.

There are two main principles:

- chemical reduction of NOx by a reducing agent with or without a catalyst,
- sorption/neutralisation of NOx.

The following secondary measures are mainly in use, each with its specific advantages and disadvantages [1]:

selective Catalytic Reduction (SCR): In SCR, NOx is reduced to N<sub>2</sub> by a reducing agent (usually ammonia) which is directly injected into the flue gas over a catalyst in the presence of sufficient oxygen. NOx-conversion takes place on the catalyst surface at a temperature between 170 and 510 degree C (with a range between 300 and 400 degree C being more typical, the minimum flue gas temperature is dependent on the sulphur content of the fuel. At a too low flue gas temperature ammonium bisulphate is formed which will clog the SCR elements. A limitation for the applicability of SCR [11] exists for diesel engines which need to be operated in varying loads. These units are operated frequently on isolated systems to be operated for a reduced number of hours only. According to the electricity demand, these engines need to be started up and shut down several times a day. SCR is an applied technique for diesel engines, but cannot be seen as BAT for engines with frequent load variation, including frequent start up and shut

down periods due to technical constraints. A SCR unit would not function effectively when the operating conditions and the consequent catalyst temperature are fluctuating frequently outside the necessary effective temperature window. As a result, SCR is part of BAT, but no specific emission levels are associated with BAT in a general sense.

• selective Non-Catalytic Reduction (SNCR): Similar to SCR a reducing agent (usually ammonia, urea or caustic ammonia) is used to reduce NOx but in contrast to SCR, without a catalyst and at a higher temperature between 850 and 1100°C.

Other secondary NOx control techniques include:

- NOXSO Process: The NOXSO process is based on simultaneous adsorption of SO<sub>2</sub> and NOx from flue gas by a regenerable sorbent, finally leading to liquid SO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>. Claimed efficiencies are 98% for SO<sub>2</sub> and 75% for NOx [9].
- SOx-NOx-Rox-Box (SNRB): SNRB uses a catalytic baghouse for integrated removal of SOx (via injection of alkali sorbent), NOx (via ammonia injection and SCR), and dust (cf 10). Problems with this technique include the production of hazardous waste as by-product and rather low abatement efficiencies.
- limestone Injection Multistage Burner (LIMB): LIMB shows lower reliability and rather low NOx abatement efficiencies.

In integrated gasification combined cycle (IGCC) the fuel is gasified under reducing conditions to syngas. The syngas is then cleaned and burnt in either air or oxygen. This enables to achieve very low NOx emission levels. IGCC is seen as one of several key technologies in the framework of carbon capture and storage (CCS). So far its application is restricted to few, mostly demonstration plants. With CCS, IGCC could become commercially available around 2020.

The selection of the most suitable measure depends on many factors related to e.g. [11]:

- fuels used,
- combustion technology applied,
- operational mode of installation,
- process characteristics in industrial processes,
- new installation or retrofitting,
- flue gas characteristics (NOx concentration, temperature, humidity, dust, other pollutants, catalyst poisons etc.),
- flow rate of flue gas,
- emission levels to be achieved,
- side and cross media effects,
- operational safety and reliability,
- costs.

The following table gives a brief overview about the performance of primary and secondary measures for reducing NOx emissions in large combustion plants; cf. the sectoral chapters for more detailed information on sector specific issues.

Technique	Average NOx reduction rate*	Technical limitations	
Low excess air (LEA)	10-44%	incomplete burn-out	
Burner out of service (BOOS)	10-70%	incomplete burn-out	
Biased burner firing (BBF)			
Overfire air (OFA)			
Flue gas recirculation (FGR)	< 20% (coal)	flame instability	
	30-50% (gas, combined with OFA)		
Reduced air preheat (RAP)	20-30%		
Fuel staging (FG)	50-60%		
Air-staged LNB	25-35%	incomplete burn-out	
		flame instability	
Flue-gas recirculation LNB	<20%	flame instability	
Fuel-staged LNB	50-60%	incomplete burn-out	
		flame instability	
Selective catalytic reduction	80-95%	ammonia slip;	
(SCR)		contamination of fly ash by	
		ammonia; air heater fouling	
Selective non-catalytic reduction (SNCR)	30-50%	ammonia slip which is usually higher than with	
		SCR	
* If several measures are applied	reduction rates are different.	•	

Table 5: average reduction efficiency of selected primary and secondary measures for reducing NOx emissions in large combustion plants for boilers [11]

#### 4.6 Costs of NOx emission reduction techniques

Costs are an important issue when selecting NOx emission reduction techniques. The following expenses may be relevant [12]:

- imputed depreciation allowance and imputed interest,
- labour costs,
- expenses for auxiliary and operating materials,
- energy costs,
- maintenance and repair costs, expenditure on monitoring, expenses for external services,
- taxes, environmental levies (e.g. charges for waste water), fees, public charges.

Costs increase in general less than the capacity of the reduction technique so that larger units are often more cost-effective. Retrofitting of existing installations is often possible but in general at higher costs.

For primary measures, investment related costs are in general relatively low and in new installations there are often no additional costs. But costs accruing from efficiency decreases may be significant and have to be accounted for.

For SCR, the cost of retrofitting may be high because of the difficulty of building a catalyst reactor close to the boiler. In addition, for SCR the following costs are most relevant: investment related costs, ammonia costs, electricity costs, catalyst replacement costs and labour costs. SNCR generally has lower costs than SCR as there are no costs for catalysts and catalyst reactor housings. However, costs for SCR and SNCR depend e.g. on the nature of the waste gas, its temperature and the required

abatement efficiency. As a consequence, the additional costs for catalyst replacement in the case of SCR may be compensated by a significantly lower ammonia consumption compared to SNCR.

# 4.7 Side effects

Side effects of emission abatement options/techniques can be positive or negative and should be accounted for. Side effects can generally be reduced by properly designing and operating the facilities. Side effects include

- impacts on energy consumption and hence greenhouse gas emissions,
- impacts on other air pollutants,
- impacts on use of natural resources,
- cross-media effects, e.g. on waste or water.

More specifically, the side effects to be considered with different emission reduction techniques are:

- **Primary measures:** possible side effects are lower overall energy efficiency, increased CO and soot formation and hydrocarbon emissions, corrosion due to reducing atmosphere, increase in unburnt carbon in fly ash.
- **FBC**: this technique also brings about a considerable reduction in  $SO_x$  emissions. A possible drawback in FBC systems may be the increased formation of  $N_2O$  under certain process conditions. The handling of the ashes needs consideration in relation to their possible use and/or disposal.
- SCR: some possible side effects are ammonia slip in the exhaust gas, ammonia content in the fly ash, formation of ammonium salts on downstream facilities, deactivation of the catalyst and increased conversion of SO<sub>2</sub> to SO<sub>3</sub> (corrosion and fouling). By the controlled operation of the plant, the fly ash quality can, however, be guaranteed and the formation of ammonia salt reduced. In terms of by-products, deactivated catalysts from the SCR process may be the only relevant products, although this has become a minor problem since catalyst lifetime has been improved and reprocessing options exist. Biomass and waste burning can reduce catalyst life.
- SNCR: side effects to be considered are ammonia in the exhaust gas, formation of ammonium salts on downstream facilities, the formation of N<sub>2</sub>O, when urea, for instance, is used as a component of the reducing mixture, and CO releases. The ammonia slip from SNCR usually is much higher than from SCR due to the required over-stoichiometric dosage of the reducing agent (at the high temperatures required for SNCR, part of the injected ammonia reacts to form additional NOx).

The **production of ammonia and urea** for flue gas treatment processes involves a number of separate steps which require energy and reactants. The storage systems for ammonia are subject to the relevant safety legislation and such systems are designed to operate as totally closed systems, with a resultant minimum of ammonia emissions. The use of  $NH_3$  is still considered appropriate, even when taking into account the indirect emissions related to the production and transport of  $NH_3$ .

#### 4.8 References used in chapter 4

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# 5 General issues for VOCs

#### 5.1 General issues

#### **Definitions**

Volatile organic compounds or VOCs means, unless other wise specified, all organic compounds of an anthropogenic nature, **other than methane**, that are capable of producing photochemical oxidant by reaction with nitrogen oxides in the presence of sunlight.

An organic compound is any compound containing at least the element carbon and one or more of hydrogen, halogens, oxygen, sulphur, phosphorus, silicon or nitrogen, with the exception of carbon oxides and inorganic carbonates and bicarbonates [1].

On case by case, other definitions can be encountered in sectoral the sections of chapter 7s:

For the uses of solvent considered in chapter 7-24 to 7-37 and technical annex VI, volatile organic compounds (VOC) mean 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 [9].

For the solvent content of products, chapter 7-38 and technical annex XI, volatile organic compounds (VOCs) means any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101.3 kPa. This definition is compatible with the previous one, as there is a relation between the boiling point and the vapour pressure.

The leak detection and repair programme (LDAR) [3] developed by the US EPA and standardised in Europe [4] is based on a vapour pressure of VOCs of 300 Pa at 295.15 K.

VOCs result from a larger number of sources both anthropogenic and natural:

- thermal processes: hydrocarbons emitted from thermal processes (fixed sources and mobile sources) contribute to the total amount of VOCs,
- use of organic solvent: an organic solvent is any VOC which is used alone or in combination with other agents, and without undergoing a chemical change, to dissolve raw materials, products or waste materials, or is used as a cleaning agent to dissolve contaminants, or as a dissolver, or as a dispersion medium, or as a viscosity adjuster, or as a surface tension adjuster, or a plasticiser, or as a preservative [1],
- transport and handling of liquid fuels and light organic compounds (petrol as example),
- refineries and organic chemical industries,
- natural sources.

VOCs play a significant role in the atmospheric chemistry. VOCs, through complex photochemical reactions, contribute to the formation of toxic oxidants, such as tropospheric ozone and other oxidants, which can trigger a variety of health problems and have detrimental effects on plants and ecosystems.

Certain VOCs have been shown to be highly toxic, mutagenic and carcinogenic. These VOCs have to receive increased attention due to their implication for human health. These VOCs are those affected by the following risk phrases [7]:

- H 350: may cause cancer;
- H 340: may cause genetic defects;
- H 350i: may cause cancer by inhalation;
- H 360F: may damage fertility;
- H 360D: may damage the unborn child.

These VOCs should be reduced as far as possible in priority. VOCs associated to risk phrases H351 suspected of causing cancerand/or H 341 suspected of causing genetic defects, should be also considered with attention and reduced as far as possible.

In order to reduce efficiently VOC emissions, it is of particular importance to consider both the reduction of stack emissions and fugitive emissions. Stack emissions refer to emissions of which the source and the direction of gas flow is clearly definable. They enter in the atmosphere by passing through a stack or a duct designed to direct and control their flow. Sources of fugitive emissions are not clearly defined. They enter in the atmosphere without passing through a stack or duct designed to direct or control the emissions. They include uncaptured emissions released to the outside environment via windows, doors, vents and similar openings [2]. In industrial plants, fugitive emissions have a diffuse character as they can arise from a lot of sources spatially dispersed.

Instead of applying emission limit values (ELV), e.g. connected to end-of-pipe measures, reduction schemes can be used. Solvent management plans have to be used as guidance for these reduction schemes. The purpose of a reduction scheme is to allow a plant operator to achieve emission reductions similar to those achieved if given limit values were to be applied by other means. Definitions of solvent management plan and of a reduction scheme are given below. Solvent management plan and reduction scheme are a key element of annexe VI to the Protocol to Abate Acidification, Eutrophication and Ground-level Ozone. They help to verify compliance with given regulations, identify future reduction options, and enable the provision of information on solvent consumption, emissions and compliance with regulations to the public.

In this guidance document, emission abatement options/techniques are characterised by:

- emission factors expressed in terms of mass of emitted substance (VOCs) or mass of total organic carbon per activity within a sector (e.g. g/m<sup>2</sup> in car coating); or
- emission factors expressed in terms of mass of emitted substance (VOCs) or mass of total organic carbon per mass of solvent input (solvent purchased + solvent recovered and reused) within a sector (e.g. % of solvent used in speciality organic chemistry); or
- concentrations in terms of mass of emitted substance (VOCs) or total organic carbon per volume unit of the exhaust gases; or
- abatement efficiency (%).

In general, no further subdivision for VOCs is made with regard to specific substances. Performance is reported where available.

# 5.2 Knowledge of emissions and solvent management plan

In order to minimise VOC emissions and construct a reduction plan, perfect knowledge of emissions is essential. This knowledge is based on monitoring VOC emissions in stacks, determining VOC fugitive emissions by several relevant techniques.

A solvent management plan is a key technique to understand the consumption, use and emissions of solvents, especially fugitive VOC emissions [5].

The solvent management plan consists in estimating solvent inputs and solvent outputs. Inputs are often easily known. On contrary, some outputs cannot be estimated easily. The solvent mass balance is a tool for estimating VOC emissions based on the following principles [1].

Definitions of inputs and outputs to be considered are as follows:

Inputs of organic solvents (I):

11 The quantity of organic solvents or their quantity in preparations purchased which are used as input into the process in the time frame over which the mass balance is being calculated.

12 The quantity of organic solvents or their quantity in preparations recovered and reused as solvent input into the process. (The recycled solvent is counted every time it is used to carry out the activity.)

Outputs of organic solvents (O):

O1 Emissions in waste gases.

O2 Organic solvents lost in water, if appropriate taking into account waste water treatment when calculating O5.

O3 The quantity of organic solvents which remains as contamination or residue in products output from the process.

O4 Uncaptured emissions of organic solvents to air. This includes the general ventilation of rooms, where air is released to the outside environment via windows, doors, vents and similar openings.

O5 Organic solvents and/or organic compounds lost due to chemical or physical reactions (including for example those which are destroyed, e.g. by incineration or other waste gas or waste water treatments, or captured, e.g. by adsorption, as long as they are not counted under O6, O7 or O8).

O6 Organic solvents contained in collected waste.

O7 Organic solvents, or organic solvents contained in preparations, which are sold or are intended to be sold as a commercially valuable product.

O8 Organic solvents contained in preparations recovered for reuse but not as input into the process, as long as not counted under O7.

O9 Organic solvents released in other ways.

Determination of solvent consumption and NMVOC emissions can be done according to equations presented here after:

Consumption can be calculated according to the following equation:

C = I1 - O8

Total NMVOC emissions are defined as follows:

E = F + O1

Where F is the fugitive emission as defined below:

F = I1 - O1 - O5 - O6 - O7 - O8

or

F = O2 + O3 + O4 + O9

This quantity can be determined by direct measurement of the quantities. Alternatively, an equivalent calculation can be made by other means, for instance by using the capture efficiency of the process.

The fugitive emission value as well as the total emission can be expressed as a proportion of the input, which is calculated according to the following equation:

| = |1 + |2|

The solvent management plan can be done on a regular basis such as an annual basis, in order to control progress carried out, take the necessary measures if deviations are observed and be in position to assess the compliance of the installation with regulation implementing ELVs.

#### 5.3 General approaches to reduce VOCs emissions

For nearly all stationary sources, measures to control or to prevent VOCs emissions are available. A distinction is generally made between primary, secondary (add-on or end-of-pipe) and structural measures. Unless stated otherwise, measures are applicable to new and existing installations. The reduction of VOC emissions outside of stationary sources focuses on the restrictions in the VOC content of products.

The following list gives a general outline of available measures for reducing VOC emissions, which may also be combined with secondary measures:

(a) More effective VOC control technologies in terms of efficient maintenance of equipment, better capture of waste gases, and generally optimized operating conditions;

(b) Substitution of VOC, e.g. use of low-organic solvent or organic-solvent-free materials and processes, such as water-based paints, water-based degreasing, etc., and/or process modifications;

(c) Reduction of emissions by best management practices such as good housekeeping, improved inspection and maintenance programmes, by changes in processes such as closed circuit machines, improved sealing of storage tanks, or by structural changes such as transfer of activity to locations where VOC emissions are reduced more efficiently, e.g. via pre-coating of certain products;

(d) Recycling and/or recovery of VOCs by control technologies such as condensation, adsorption, absorption, and membrane processes (pre-processing step). A further option is the recovery of heat (energy recovery) from VOCs. Preferably, the organic compounds should be reused on-site; this can

be facilitated by the use of only few organic solvents instead of complex mixtures. Complex mixtures may be better treated off-site; however, emissions may be caused by distribution, handling, transport and storage;

(e) Destruction of VOCs by control technologies such as thermal or catalytic incineration, or biological treatment. For incineration, heat recovery is recommended in order to reduce operating costs and resource consumption. Another common procedure for destroying non-halogenated VOCs is to use VOC-laden gas streams as secondary air or fuel in existing energy-conversion units.

#### 5.3.1 Primary measures

Possible primary measures for the control of emissions from the industrial use of organic solvents are: prevention (use of low- or no-organic solvent containing materials and processes), good housekeeping, process-integrated measures and structural measures. Thus, two approaches can in principle be used: a product-oriented approach, which, for instance, leads to a reformulation of the product (paints, inks, degreasing products, etc.); and process-oriented changes (increase of transfer efficiency, use of sealed chamber systems for degreasing...); other); Moreover, the product-oriented approach should be looked at, inter alia, because of the positive spin-off effects on emissions from the organic solvents manufacturing industry. Moreover, the environmental impact of emissions can be reduced by product reformulation to replace solvents by less harmful alternatives. Closed systems are lead to very low organic solvent emissions as well. There is a rapid ongoing development towards low-organic solvent or organic-solvent-free paints, which are among the most cost-effective solutions.

For the domestic use of paints and other solvent-containing products, only a product-oriented approach is possible. The same is true for the painting of constructions and buildings, the commercial use of cleaning products, etc. The use of water-based systems (e.g. for paints and adhesives) is an effective measure already used, especially for products for both commercial and domestic purposes.

#### 5.3.2 Secondary measures

When primary measures are not sufficient to reach high VOC reductions or are not technically applicable, add-on control technologies can be applied alone or in combination. These techniques are used to reduce VOC emissions from processes and solvent uses.

The following techniques can be distinguished:

- techniques based on destruction of VOCs present in waste gases:
- recuperative or regenerative thermal oxidation,
- catalytic recuperative or regenerative oxidation,
- biological destruction.
- techniques enabling possible recovery of VOCs for possible reuse in the process after a specific treatment carried on site or by external companies:
- adsorption on activated carbon or zeolithe substrates,
- absorption in adapted scrubbing liquors (water, heavy oils),
- condensation and cryogenic condensation,
- membrane separation associated to other processes such as cryogenic condensation and adsorption.

Processes using thermal oxidation may enable valorisation of the energy content of VOCs. However, in most cases, this valorisation is difficult due to the low VOC concentrations generally encountered. Primary thermal energy recovery (for warming inlet gases as example) is indispensable but secondary thermal energy recovery is often most difficult to be implemented in existing plants. The VOCs concentrations have to be sufficient for enabling the oxidation unit to run without additional fuel consumption and to be consequently in autothermal conditions. Lower concentrations require additional fuel consumption which can be rapidly prohibitive.

**Recuperative or regenerative thermal oxidation**. In recuperative or regenerative oxidation, VOCs are destructed at high temperature. The oxidation temperature depends on the type of energy recovery system used. In recuperative oxidiser, a preheating thermal exchanger is used to heat inlet gases. The heat recovery ranges from 60 to 70 %. The temperature ranges from 650 to 750°C. The system can only be autothermal for high concentrations of VOCs ranging from 8 to 10 g/Nm<sup>3</sup>. The regenerative thermal oxidiser is constituted of two or three ceramic heat exchangers. Waste gases containing VOCs pass through a first ceramic exchanger. They are heated. They enter after in the combustion chamber maintained at about 800 to 900 °C by burners. Before being released into the atmosphere they leave the oxidiser through another ceramic exchanger, transferring its thermal energy to be re-used for preheating the next cycle. The role of the exchanger, heating or cooling, is inversed regularly. Heat recovery efficiency up to 95 % can be achieved. Regenerative thermal oxidisers are suitable for large waste gas flow rates and can be autothermal at VOCs concentrations from 2 to 3 g/Nm<sup>3</sup>. Output VOC concentrations lower than 20 mg/Nm<sup>3</sup> can be achieved in perfectly dimensioned and operated oxidisers. Methane is largely represented in the resulting concentrations.

**Recuperative or regenerative catalytic oxidation.** In recuperative or regenerative catalytic oxidation, the use of a catalyst enables VOCs to be destroyed at lower temperature than in thermal oxidation. Catalysts used are either precious metals (Platinum, Palladium or rhodium) or metal oxides (Cr, Fe, Mo, Mn, Co, Cu, Ni). The principles of heat exchange are the same as in thermal oxidation. Oxidation temperatures range from 200 to 500 °C according to catalyst used and the type of heat exchanger used. Recuperative catalytic oxidiser can be autothermal at concentrations ranging from 3 to 4 g/Nm<sup>3</sup>. Regenerative catalytic oxidiser can be autothermal at concentrations ranging from 1 to 2 g/Nm<sup>3</sup>. Life time of catalysts is limited. Lifetime of metal oxide based catalysts is about 12 000 h. Life time of precious metal based catalysts is about 15 000 h to 25 000 h. Catalysts are sensible to poisons and they can be achieved in perfectly dimensioned and operated oxidisers. When using liquid fuels with more than 0.1% S in the power plant prime mover, the catalyst lifetime can be shortened. Methane is largely represented in the resulting concentrations.

**Biological destruction:** biological destruction can be carried out in bio filters and in bio scrubbers. Micro organisms are able to destruct biodegradable VOCs in humid conditions and at low temperature. Warm waste gases (> 35 °C) must be cooled. In bio filter, microorganisms are maintained at the surface of a moist organic substrate which can be peat, heather or compost. In bio scrubbing, a combination of wet gas scrubbing and biodegradation is carried out. Microorganisms are suspended in the scrubbing water. In biofilters, residence time must be sufficient to enable biological reactions to occur. Accepted inlet VOC concentrations are low. Biological oxidation is used primarily for low concentrations. Output VOC concentrations from 100 to 150 mg/Nm<sup>3</sup> can be achieved. Lower concentrations are however more difficult to obtain.

Adsorption on activated carbon or zeolithes. In adsorption, VOCs are physically bound to the surface of a media which can be activated carbon or zeolithes. The adsorption capacity of activated carbon or zeolithe is limited and consequently they must be regenerated to recover their initial capacity to adsorb VOCs and recover VOC. Several configurations exist but in most of the cases, fixed bed adsorption devices are used with 2 or 3 beds. A bed is in adsorption phase, the second one is in desorption phase. Desorption is carried at high temperature with steam or inert gas. The adsorption temperature must be below 40 °C because the effectiveness of adsorption improves at low temperature. Inlet gases must be consequently conditioned. VOCs are recovered after a special treatment which involves condensation, separation and distillation if several VOCs are present. VOCs abatement efficiency depends on a lot of parameters such as adsorption temperature, type and number of VOCs to be eliminated, frequency set point for desorption. Output VOC concentrations from 50 to 100 mg/Nm<sup>3</sup> can be achieved. Efficiencies achieved depend on numerous factors such as correct dimensioning of the installation, the frequency of desorption and the threshold value fre-for desorption.

**Condensation and cryogenic condensation:** in condensation VOCs are cooled below the stream dew point. Condensation of VOCs is carried out by chilling and /or pressurisation. Cooling media can be cooled water, chilled water, refrigerants and liquid nitrogen. Diverse heat exchangers equipment can be used. Condensation with cooled water, chilled water or refrigerants is often used as pre-

treatment but is not sufficient to achieve high reduction of emissions. Output VOC concentrations from 100 to 150 mg/Nm<sup>3</sup> can be achieved. Efficiencies achieved depend on numerous factors such as correct dimensioning of the installation, the frequency of desorption and the threshold value for desorption...

Liquid nitrogen is used in cryogenic (temperature less than -160°C) condensation. Cryogenic condensation is a versatile process that is not VOCs specific. Typically, condensation takes place with liquid nitrogen as the refrigerant in a straightforward heat exchange process. The VOCs condense on the shell side of the exchanger then drains into a collection tank, from which it can be recycled, reclaimed, recovered for reuse or for disposal. During condensation, the presence of water vapour or VOCs with a high melting point can cause freezing on the external surface of the tubes inside a cryogenic condenser. Special configuration exists to avoid this problem and especially a series of condenser can be used with different temperature set points [8]. Cryogenic condensation is best suited to low waste gas flowrates and/or high VOCs concentrations. Output VOC concentrations from 50 to 100mg/Nm<sup>3</sup> can be achieved. Efficiencies achieved depend on numerous factors such as correct dimensioning of the installation, the volatility of solvents...

**Membrane separation:** VOC emissions can be concentrated using organic selective (VOCs permeable) membranes. Air and VOCs permeate through the membrane at rates determined by their relative permeabilities and the pressure difference across the membrane. Membranes are typically 10 to 100 times more permeable to VOCs than air, depending on the specific VOC characteristics. Based on the system design, the exit membrane stream VOC concentration can be increased five to fifty times the inlet membrane stream concentration. Concentrated gas streams can be then compressed and condensed by the use of conventional condensation technology. Membrane separation cannot be used alone. Subsequent gas cleaning device is necessary.

The choice of a control technique will depend on various parameters, such as the concentration of VOCs in the raw gas, the gas volume flow, the type and composition of VOCs, and others. Therefore, some overlap in the fields of application may occur. In that case, the most appropriate technique must be selected according to case-specific conditions. An overview of the most relevant parameters for the application of some secondary measures is outlined in table  $\frac{26}{2}$ . The overall efficiency of secondary measures in the solvent-using sectors depends to a large extent on the capturing efficiency for the VOC-laden waste gas flows. Especially for fugitive emissions, capturing is paramount for the overall efficiency of the system.

	Thermal recuperative oxidation	Thermal regenerative oxidation	Catalytic recuperative oxidation	Catalytic regenerative oxidation
Ranges of concentrations	Adapted to high concentrations 5 to 20 g/Nm <sup>3</sup>	Adapted to low concentrations 2 to 10 g/Nm <sup>3</sup>	Adapted to low concentrations 2 to 10 g/Nm <sup>3</sup>	Adapted to very low concentrations C < 5 g/Nm <sup>3</sup>
Waste gas flow rates	1 000 to 30 000 Nm <sup>3</sup> /h	10 000 to 200 000 Nm <sup>3</sup> /h	1 000 to 30 000 Nm <sup>3</sup> /h	10 000 to 100 000 Nm <sup>3</sup> /h
Authothermic threshold	8 to 10 g/Nm <sup>3</sup>	2 to 3 g/Nm <sup>3</sup>	3 to 4 g/Nm <sup>3</sup>	1 to 2 g/Nm <sup>3</sup>
Performances				
VOCs (C eq) NOx <sup>1</sup> CO	< 20 mg/Nm <sup>3</sup> < 100 mg/Nm <sup>3</sup> < 100 mg/Nm <sup>3</sup>	< 20 mg/Nm <sup>3</sup> < 50 mg/Nm <sup>3</sup> < 50 mg/Nm <sup>3</sup>	< 20 mg/Nm <sup>3</sup> < 50 mg/Nm <sup>3</sup> < 50 mg/Nm <sup>3</sup>	< 20 mg/Nm <sup>3</sup> < 50 mg/Nm <sup>3</sup> < 50 mg/Nm <sup>3</sup>
Limits of uses	Low concentrations Presence of halogenated organic compounds ;	of halogenated organic organic compounds ; Presence of Presence of compounds ;		Presence of halogenated organic compounds ; Presence of catalyst poisons ;
	Energy consumption outside autothermal conditions.	particulate matter ;	poisons ; Presence of Particulate matter ; Risks of high concentrations	Presence of Particulate matter ; Risks of high concentrations

## Table 6: overview of the most relevant parameters for the application of secondary measures

	Biological destruction	Adsorption on activated carbon	Absorption in heavy oil	Cryogenic condensation
Ranges of concentrations	Adapted to very low concentrations C < 1 à 2 g/Nm <sup>3</sup>	C < 15 g/Nm <sup>3</sup>	C < 10-15 g/Nm <sup>3</sup>	C > 10 g/Nm <sup>3</sup>
Waste gas flow rates	1 000 à 100 000 Nm³/h	1 000 to 100 000 Nm <sup>3</sup> /h	1 000 to 100 000 Nm <sup>3</sup> /h	1 000 to 5 000 Nm³/h
Performances (C eq)	100-150 mg/Nm <sup>3</sup>	50 to 100 mg/Nm <sup>3</sup>	50 to 100 mg/Nm <sup>3</sup>	50 to 100 mg/Nm <sup>3</sup>
Limits of uses	non biodegradable VOCs, Temperature of waste gases to be treated Non permanent release of NMVOC.	Number of VOCs Presence of particulate matter ; Presence of polymerisable compounds ; Treatment of recovered products.	Number of VOCs Capacity of absorption of VOCs; Treatment of recovered products.	Number of VOCs High volatile compounds Humidity ; Treatment of recovered products.

<sup>1</sup>Concentrations obtained for oxidisers used to abate VOC emissions from solvent uses in processes.

## 5.4 Costs

The estimation of investments and operating costs for VOC emission reduction options/techniques is important when choosing from the wide range of measures and, on a macroeconomic level, when developing a national or regional emission control strategy. It must be borne in mind that specific figures are highly dependent on factors such as plant capacity, removal efficiency, VOC concentration in the raw gas, type of technology, and the choice of new installations as opposed to retrofitting. These parameters, and thus the costs incurred as well as the resulting ranking of measures in terms of costs, may be highly case-specific, for instance for retrofit cases, and examples should not be generalised.

EGTEI documents defining the methodologies used to estimate costs for waste gas treatment techniques are available. Documents on oxidation, carbon adsorption and bio filtration are available at: <a href="http://citepa.org/forums/egtei/egtei\_doc-VOC\_abattement\_tech.htm">http://citepa.org/forums/egtei/egtei\_doc-VOC\_abattement\_tech.htm</a>.

Investments and operating costs depend particularly on flow rates and VOC concentrations to be treated. Costs are provided in chapter 7.

## 5.5 Side effects

Side effects of emission abatement options/techniques can be positive or negative and should be accounted for. Side effects can generally be limited by properly designing and operating the facilities. Side effects include:

- impacts on energy consumption and hence greenhouse gas emissions,
- impacts on other air pollutants,
- impacts on the use of natural resources,

• cross-media effects, e.g. on waste or water.

Table 7: positive and negative side effects of VOC emission reduction techniques

Reduction technique	Positive side effects	Negative side effects
Oxidation	Possible co-treatment of odours	Energy consumption and GHG emissions in case of non autothermal conditions
Adsorption	Possible co-treatment of odours	Possible increase of energy consumption for steam generation
Cryogenic condensation	Possible co-treatment of odours	Energy consumption to produce liquid nitrogen

## 5.6 References used in chapter 5

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EPA 453-95-017 – 1995

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"Fugitive and diffuse emissions of common concern to industry sectors - Measurement of fugitive emission of vapours generating from equipment and piping leaks"

European comity of normalisation

[5] European Commission - reference document on BAT in surface treatment with solvent 2007

[6] European Commission - reference document on BAT in common waste water and waste gas treatment / management systems in the chemical sector – February 2003.

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[8] Joint Service Pollution Prevention and Sustainability Technical Library

http://205.153.241.230/topics/airpollution.html

Mis en forme : Non Surlignage Mis en forme : Non Surlignage

## 6 General issues for dust (including PM<sub>10</sub>, PM<sub>2,5</sub> and BC).

## 6.1 General issues

Dust refers to a complex mixture of small to tiny particles and liquid droplets suspended in air. Sizes of dust range from several nanometers up to 100 micrometers ( $\mu$ m). Dust may be differentiated according to the aerodynamic diamete,r into:

- large particles with an aerodynamic diameter of more than 10 μm,
- coarse particles with an aerodynamic diameter of 2.5 to 10 μm,
- fine particles with an aerodynamic diameter of less than 2.5 µm,
- ultrafine particles with an aerodynamic diameter of less than 0.1 µm,

and more particularly into:

- Total Suspended Particles (TSP) as the sum of fine, coarse and large particles,
- PM<sub>10</sub>: the mass of particulate matter that is measured after passing through a size-selective inlet with a 50 % efficiency cut-off at 10 µm aerodynamic diameter,
- PM<sub>2.5</sub>: the mass of particulate matter that is measured after passing through a size-selective inlet with a 50 % efficiency cut-off at 2.5 μm aerodynamic diameter;
- PM<sub>1</sub>: the mass of particulate matter that is measured after passing through a size-selective inlet with a 50 % efficiency cut-off at 1 µm aerodynamic diameter.

Besides this size dependent classification, dust is also differentiated according to its origin into primary and secondary dust. Dust can be natural (sea salts, volcanoes, soil erosion...), <u>etc</u> and anthropogenic (combustrion, processes...), <u>etc</u>). According to its source, dust has different chemical compositions. Primary dust is composed of salts (nitrates, sulphates, carbonates...), <u>etc</u>), of black carbon (BC), of organic carbon (non-carbonate carbonaceous particles other than elemental carbon [20]) (OC) and trace elements such as heavy metals. Secondary PM is formed in the atmosphere of the precursors ammonia, sulphuric acid, nitric acid and NMVOC-related organic oxidation products [1].

Dust affects the radiation balance of the earth. Some components of dust have a cooling effect (sulphates, OC). Other ones, have a warming effect (BC).

BC means carbonaceous particulate matter that absorbs light. Absorption occurs at all wavelengths of solar radiation [16], [19]. BC remains in the atmosphere for days to weeks and because of its light absorbing properties, it contributes significantly to global warming. It also darkens snow and ice after deposition and thereby reduces the surface albedo, or reflectivity. This albedo effect is particularly prevalent in the Arctic region. By darkening ice and snow, it contributes to regional warming [16], [17], [18].

The BC content of dust increases with incomplete combustion of various fossil fuels, biofuels and biomass [16]. BC is part of a complex particle mixture called soot which primarily consists of BC (which is a warming agent) and OC (which is a cooling agent). There is a close relationship between the two compounds. They are always co-emitted, but in different proportions for different sources. Soot mixtures can vary in composition, having different ratios of OC to BC and usually include inorganic materials such as metals and sulphates. For example, the average OC/BC ratio of diesel exhaust could range approximately from 1/4 (heavy duty engine type operating on distillate) according to reference [19] to 15/1 (large medium speed engine operating on heavy fuel oil) according to reference [2434]. For biofuel burning, the ratio is approximately 4/1 and for open vegetation fires (or open biomass burning) it is approximately 9/1 [19]. For all sources, monitoring results are needed to improve knowledge of BC emissions.

BC forms during combustion, and is emitted when there is insufficient oxygen and heat available for the combustion process to burn the fuel completely. BC originates as tiny spherules, ranging in size from 0.001 to 0.005 micrometers ( $\mu$ m), which aggregate to form particles of larger sizes (0.1 to 1  $\mu$ m). The characteristic particle size range, in which fresh BC is emitted, also makes it an important constituent of the ultrafine particles (<100 nanometers (nm)). BC is associated with particles less than 1  $\mu$ m [19]. When combustion is carried out in optimal O<sub>2</sub> concentrations (optimal excess air) and optimal temperatures, mainly salts are present in dust. Mitigation techniques for BC are the same as for PM<sub>2.5</sub> as BC is a compound of dust. Only fabric filters and electrostatic precipitators can be efficiencies on fine particles.

Inhaling dust may cause negative health effects [2] like asthma, lung cancer, cardiovascular issues, and premature death. Health effects are related to particle size as large particles can be filtered out in the nose and throat. Particles with a size less than about 10  $\mu$ m can enter the bronchi and the lungs, particles less than 2.5  $\mu$ m in diameter the gas-exchange regions of the lung, and particles less than 0.1  $\mu$ m can enter via the lungs into other organs. Therefore, the potential for negative health effects increases with decreasing particle diameter. Besides particle size also the chemical composition, e.g. carcinogenic components, and solubility of the particle in the lung has an impact on the potential health effects. Health effects are expected to be related to the number of smaller particles whereas most measurements refer to the particle mass which is in general dominated by the larger particles within the size fraction.

Furthermore, dust generates haze with effects on visibility.

For dust, there are several natural and anthropogenic sources with differences in the size and the chemical composition of the generated dust. Dust formation may result from:

- mechanical processing of solid matter (crushing, grinding, surface processing, abrasion etc.),
- chemical and physical reactions (incomplete combustion, gas-to-particle conversion, condensation, deposition etc.),
- exposure of solid matter (wind erosion etc.)
- re-suspension of dust (from roads, stockpiles etc.).

Published measurement data on the share of  $PM_{2.5}$  and  $PM_{10}$  in waste gas is scarce and/or of limited quality. Therefore the following tables citing calculated shares as used in the RAINS/GAINS model are presented.

Sector Name	RAINS-Code(s)	Unit	PM2.5	% PM2.5	PM10	%PM10	TSP
Coal, grate (in industry, raw gas)				7%		20%	
Coal, fluidized (in industry, raw gas)				5%		26%	
Brown coal, pulverized (in industry, raw gas)				10%		35%	
Hard coal, pulverized (in industry, raw gas)				6%		23%	
Derived coal (in industry, raw gas)				45%		79%	
Biomass (in industry, raw gas)				77%		89%	
Waste (in industry, raw gas)				23%		38%	
Coal, grate (in power plants, raw gas)				14%		37%	
Coal, fluidized (in power plants, raw gas)				5%		26%	
Brown coal, pulverized (in power plants, raw gas)				10%		35%	
Hard coal, pulverized (in power plants, raw gas)				6%		23%	
Hard coal, wet bottom (in power plants, raw gas)				21%		23%	
Derived coal (in power plants, raw gas)				45%		79%	
Biomass (in power plants, raw gas)				77%		89%	
Waste (in power plants, raw gas)				23%		38%	
Coal, stoves and boilers (domestic)				13%		90%	
Coal, large boilers (residential)				7%		20%	
Derived coal (residential)				45%		79%	
Biomass, stoves and boilers (domestic)				93%		96%	
Biomass, large boilers (residential)				77%		89%	
Waste (residential)				60%		90%	
Fireplaces, stoves (wood burning in Eastern Europe)	DOM_FPLACE, DOM_STOVE	kt/PJ	0,279	93%	0,288	96%	0,3
Small domestic boilers (wood burning in Eastern Europe)	DOM_SHB_M, DOM_SHB_A	kt/PJ	0,093 - 0,23	37% - 92%	0,096 - 0,24	37% - 96%	0,1 - 0,25
Large residential boilers (wood burning in Eastern Europe)	DOM_MB_M, DOM_MB_A	kt/PJ	0,077 - 0,15	39% - 75%	0,089 - 0,18	45% - 90%	0,1 - 0,2
Industry (wood burning in Eastern Europe)	PP_, IN_, CONV_COMB	kt/PJ	0,185	77%	0,214	89%	0,24
Fireplaces, stoves (wood burning in Western Europe)	DOM_FPLACE, DOM_STOVE	kt/PJ	0,067 - 0,186	34% - 93%	0,07 - 0,192	35% - 96%	0,072 - 0,2
Small domestic boilers (wood burning in Western Europe)	DOM_SHB_M, DOM_SHB_A	kt/PJ	0,06 - 0,167	33% - 93%	0,062 - 0,17	34% - 94%	0,065 - 0,18
Large residential boilers (wood burning in Western Europe)	DOM_MB_M, DOM_MB_A	kt/PJ	0,05 - 0,12	33% - 80%	0,06 - 0,134	40% - 89%	0,065 - 0,15
Industry (wood burning in Western Europe)	PP_, IN_, CONV_COMB	kt/PJ	0,185	77%	0,214	89%	0,24

## Table 7: shares of $PM_{2.5}$ and $PM_{10}$ in TSP as used in RAINS (2002) [15]

Table 7. Shares of $FM_{2.5}$ and $FM_{10}$ in TSF as used in RAINS (2002) [15]							
Sector Name	RAINS-Code(s)	Unit	PM2.5	% PM2.5	PM10	%PM10	TSP
Power plants (stationary combustion of heavy fuel oil)	PP_NEW, PP_EX	kt/PJ	0,0093	60%	0,0132	85%	0,0155
Conversion (stationary combustion of heavy fuel oil)	CON_COMB	kt/PJ	0,0117	60%	0,0166	85%	0,0195
Industry (stationary combustion of heavy fuel oil)	IN_BO, IN_OC	kt/PJ	0,0104	60%	0,0147	85%	0,0173
Residential (stationary combustion of heavy fuel oil)	DOM	kt/PJ	0,0095	25%	0,0247	65%	0,038
Power plants (stationary combustion of light fuel oil), new	PP_NEW	kt/PJ	0,0004	18%	0,0011	50%	0,0022
Power plants (stationary combustion of light fuel oil), existing	PP_EX	kt/PJ	0,0007	19%	0,0018	50%	0,0036
Conversion (stationary combustion of light fuel oil)	CON_COMB	kt/PJ	0,0004	11%	0,0018	50%	0,0036
Industry (stationary combustion of light fuel oil)	IN_BO, IN_OC	kt/PJ	0,0003	14%	0,0011	50%	0,0022
Residential (stationary combustion of light fuel oil)	DOM	kt/PJ	0,0007	41%	0,0009	53%	0,0017
Power plants (stationary combustion of natural gas)	PP_NEW, PP_EX	kt/PJ	0,0001	100%	0,0001	100%	0,0001
Conversion (stationary combustion of natural gas)	CON_COMB	kt/PJ	0,0001	100%	0,0001	100%	0,0001
Industry (stationary combustion of natural gas)	IN_BO, IN_OC	kt/PJ	0,0001	100%	0,0001	100%	0,0001
Residential (stationary combustion of natural gas)	DOM	kt/PJ	0,00003 - 0,0002	100%	0,0000 3 - 0,0002	100%	0,00003 - 0,0002
Coke Production	PR_COKE	kt/ton	1,9971	40%	3,3618	68%	4,976
Sinter processes	PR_SINT	kg/ton sinter	0,557	7%	1,285	15%	8,563
Sinter fugitive	PR_SINT_F	kg/ton sinter	0,104	7%	0,24	15%	1,6
Pellet plant	PR_PELL	kg/ton pellet	0,03	100%	0,03	100%	0,03
Pig iron production	PR_PIGI	kg/ton pig iron	0,15	10%	0,24	16%	1,48
Pig iron production (fugitive)	PR_PIGI_F	kg/ton pig iron	0,15	6%	0,25	10%	2,5
Open-hearth furnace	PR_HEARTH	kg/ton steel	6,33	60%	8,76	83%	10,55
Basic oxygen furnace	PR_BAOX	kg/ton steel	10,45	50%	14,63	70%	20,9
Electric arc furnace	PR_EARC	kg/ton steel	7,55	43%	10,18	58%	17,55
Iron foundries	PR_CAST	kg/ton iron	10,68	71%	13,55	90%	15,05
Iron foundries (fugitive)	PR_CAST_F	kg/ton iron	1,38	24%	2,82	49%	5,75
Aluminium production (primary)	PR_ALPRIM	kg/ton aluminium	18,5	39%	27,26	58%	47
Aluminium production (secondary)	PR_ALSEC	kg/ton aluminium	5,195	44%	6,93	58%	11,9
Other Non-ferrous metals	PR_OT_NFME	kg/ton metal	12,3	82%	13,8	92%	15
Cement production	PR_CEM	kg/t cement	23,4	18%	54,6	42%	130
Lime production	PR_LIME	kg/t lime	1,4	1%	12	12%	100
Petroleum refining (refineries)	PR_REF	kg/t crude oil	0,096	79%	0,12	98%	0,122
Fertilizer production	PR_FERT	kg/t	18	36%	30	60%	50
Carbon Black production	PR_CBLACK	kg/t	1,44	81%	1,6	90%	1,78
Glass production	PR_GLASS	kg/t glass	2,96	91%	3,09	95%	3,25
Other production (PVC, gypsum, glass fibre)	PR_OTHER	kg/ton product	0,5 - 8	3% - 46%	2 - 15	11% - 86%	5 - 17,5

Table 7: shares of $PM_{2.5}$ and $PM_{10}$ in TSP as used in R	AINS (2002) [15]
14410 11 014100 01 1 112.5 4114 1 11110 110 100 400 400 400 400 40	

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Major stationary sources of dust emissions are therefore combustion processes, in particular of coal, fuel oil and biomass but also of black liquor in paper industry, industrial processes like sintering, cement production etc. as well as storage, handling and mechanical processing of materials.

BC emission inventories are available at the global scale or local level. Reference [21] provides an overview of available inventories [22], [23], [24], [25] at the global scale. The GAINS model has been extended to cover BC and OC [27]. A report on emission factor determination is available from IIASA [26]. Uncertainties are still considerable regarding sources such as combustion, agricultural burning, and open biomass burning (wild fire and prescribed forest burning), however there is a consensus on the most important sources of BC. These sources are [17], [19]:

In UNECE regions:

- the on-road and off-road diesel engines including marine engines;
- the domestic sector due to emissions from domestic heating, primarily wood but also coal combustion;
- the open biomass burning sector, primarily due to emissions from agricultural burning, prescribed burning in forestry, and wildfires.

Globally, important sources include residential cook stoves in all regions; brick kilns and coke ovens in Asia; and mobile diesel vehicles and marine engines in all regions; open biomass burning in all regions. Gas flaring from fossil fuel extraction is also considered as a significant BC emission source by most publications.

The following graph presents emission sources in the UNECE region according to GAINS [28]. In this region, residential combustion (biomass and coal), road traffic and off-road machineries are the largest sources of BC. Off-road sources are very significant as well as open biomass burning in agricultural activities.

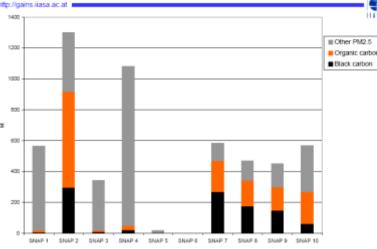


Figure 1: BC and OC emission sources in the UNECE region according to GAINS [28]

SNAP 1: combustion in energy and transformation industries

SNAP 2: non industrial combustion plants SNAP 3: combustion in manufacturing industries

SNAP 4: production processes

SNAP 5: extraction and distribution of fossil fuels and geothermal energy

SNAP 6: solvent and other product use

SNAP 7: road transport

SNAP 8: other mobile sources and machinery

SNAP 9: waste treatment and disposal

SNAP 10: agriculture

In order to reduce dust formation and dust emissions different types of measures like energy efficiency improvements (cf. Chapter 2.2), fuel switching, fuel cleaning, better handling of materials as well as

abatement measures are applied. To achieve the most efficient dust reduction, beyond energy management measures, a combination of measures should be considered. To identify the best combination of measures a site-specific evaluation is needed.

## 6.2 Fuel switching

Fuel switching is an important option to reduce dust emissions from combustion but is governed by country specific conditions such as infrastructure and energy policy. Dust emissions are in general lower if the fuel allows a more homogenous combustion, contains less sulphur and less ash but more hydrogen. Therefore, combustion of natural gas is in general associated with low emissions whereas high dust emissions result from combustion of fuel oil, biomass and coal if no abatement measures are applied.

BC mainly results from incomplete combustion. The form of the fuel influences the likelihood of complete combustion and the reduction of BC can be achieved through fuels able to limit the occurrence of incomplete combustion [19]:

Gas phase fuels (e.g., natural gas) can be readily mixed with oxygen, which reduces the emission of carbonaceous particles.

Liquid fuels (e.g., gasoline) generally must vaporize in order to fuel flaming combustion. If a liquid fuel contains heavy oils, vaporisation and thorough mixing with oxygen are difficult to achieve.

Solid fuels (e.g., wood) require preheating and then ignition before flaming combustion can occur. High fuel moisture can suppress full flaming combustion, contributing to the formation of Brown Carbon (Bra) particles as well as BC.

The choice of the fuel may also have effects on other emissions like sulphur, NOx and greenhouse gas emissions as well as on applicability and need of abatement measures.

## 6.3 Fuel cleaning

Fuel cleaning is important for coal and fuel oil.

Conventional coal cleaning techniques rely on gravity-based separation of ash and sulphur compounds using jigs, dense-medium baths, cyclones or flotation of grinded coal. While 60 to 90% and 85 to 98% of the heating value of the coal is retained, ash removal can reach 60% and total sulphur removal 10 to 40%. Both sulphur and ash removal contributes to a reduction of dust emissions. Sulphur removal increases with the content of pyritic sulphur in the coal [4]. Advanced techniques are mostly based on:

- advanced physical cleaning (advanced froth floatation, electrostatic, heavy liquid cycloning),
- aqueous phase pre-treatment (bioprocessing, hydrothermal, ion exchange),
- selective agglomeration (Otisca, LICADO, spherical agglomeration Aglofloat),
- organic phase pre-treatment (depolymerisation, alkylation, solvent swelling, catalyst addition (e.g., carbonyl), organic sulphur removal).

These advanced coal cleaning techniques are still in development or demonstration phase [4]. Besides a reduction of sulphur and dust emissions, reported advantages are lower transportation costs if coal is cleaned already at the mine, higher boiler availability, less boiler slagging and fouling, less wear on equipment, lower dust load. Disadvantages are energy loss from cleaning (2-15%), energy costs for the processes and an increased moisture content of the coal if water-based processes are used [4].

Fuel desulphurisation for fuel oil is common practice in order to achieve low sulphur fuels which are e.g. required in the EU by Directive 1999/32/EC (heavy and light fuel oil less than 1% resp. 0.1% wt). Removing of sulphur reduces sulphur based dust emissions (Chapter 3.4 describes the desulphurisation processes of fuel oils).

## 6.4 Primary measures

### Unloading, handling and storage of solids

During unloading, storage and handling, e.g. loading, of solids dust emissions might occur. In general particle size of dust from unloading, storage and handling of solid is larger than dust from e.g. combustion. The use of enclosed or housed systems, e.g. covered continuous conveying systems, and reducing of drop heights may reduce dust emissions from unloading and handling [3]. Approaches to minimise dust from storage can be differentiated into primary measures which reduce emissions and secondary measures which aim at limiting the distribution of the dust [2]. Primary measures can be further differentiated into organisational, constructional, and technical measures. Technical primary measures are wind protection, covering or avoidance of open storage, and moistening of the open storage, e.g. by a sprinkler systems. Secondary measures are spraying, water curtains and jet spraying as well as installation of filters in e.g. silos [2]. Spraying water is also a measure to reduce dust emissions from construction sites.

### Capture of emissions

A prerequisite for later dust abatement is the capture of fugitive dust emissions, e.g. in the iron and steel industry, and venting to dust control systems.

### Combustion technique and optimisation

A smooth, continuous and complete combustion generates less dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and black carbon) emissions. An optimised air supply, mixing of fuel and air as well as burner/boiler design reduce the formation of soot and other substances resulting from incomplete combustion such as BC. Therefore good housekeeping of boilers as well as the use of new, more efficient boilers and stoves, especially in the residential and commercial sector, may reduce dust and BC emissions. In this way dust and BC emissions from wood <u>and coal</u> stoves can be considerably reduced. Changing from batch to continuous operation of boilers allows for a better combustion control and reduces dust and BC emissions. Primary measures for NOx reduction may, however, increase soot formation (cf. Chapter 4) A lowering of the combustion temperature reduces and volatisation. Fuel additives and sorbents are proposed to reduce the formation of fine particles and metals in the fine particles. In Integrated gasification combined cycle (IGCC) the fuel is gasified under reducing conditions to syngas. The syngas is then cleaned and burnt in either air or oxygen. This allows the achievement of very low dust emission levels. IGCC is seen as one of several key technologies in the framework of carbon capture and storage (CCS). So far its application is restricted to few, mostly demonstration plants. With CCS-IGCC could become commercially available around 2020 [5].

## 6.5 Secondary measures

Secondary measures (add-on or end of pipe technologies) reduce the emissions of PM which is already in the flue gas. Several main principles are used for secondary measures:

- inertia of particles,
- sieving and adsorption,
- electrostatic charging of particles and subsequent precipitation making use of an electric field,
- scrubbing.

The following secondary measures<sup>1</sup> are mainly in use, each with its specific advantages and disadvantages according to the size of particles. Because BC from incomplete combustion is mainly associated to particles with a diameter less than 1  $\mu$ m, only reduction techniques able to remove fine particles will have a significant efficiency on BC emissions:

 gravity settling chamber: In gravity settling chambers the flow rate of the air is reduced so that larger particles sink and settle. Gravity settling chambers are only useful for removing the largest particles in terms of "pre-cleaning". The minimum particle size removed by gravity settling chambers is >20 µm [1]. Table 8 presents dust removal efficiencies of gravity settling chamber. This equipment is not suitable for removal of fine particle and BC.

<sup>1</sup> The performance data in the following paragraphs mainly refer to boiler installations

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- cyclone: In cyclones inertia of particles are used for dust removal. In a cyclone the flue gas is forced (usually via a conical shaped chamber) into a circular motion where particles are forced by inertia to the cyclone walls where they are collected. Collection efficiency depends strongly on particle size and increases with the pollutant loading. For conventional single cyclones it is estimated to be 70-90% for TSP, 30-90% for  $PM_{10}$  and 0-40% for  $PM_{2.5}$  [6]. The minimum particle size removed by cyclones is 5-25 µm and 5 µm in multicyclones [1]. Conventional cyclones are therefore referred to as "pre-cleaners". Conventional cyclones alone are not BAT for industrial installations but could be an option to reduce dust emissions from small combustion installations, e.g. in households or in the commercial sector. High efficiency cyclones removing 60-95% of PM10 and 20-70% of PM2.5 have been developed but at the expense of a high pressure drop leading to high energy and hence operation costs [6]. Achieving higher removal efficiencies in cyclones is mainly a problem of the resulting pressure drop. High throughput cyclones have been designed on purpose for removing just the larger dust fraction at the expense of only low pressure drop. In multicyclones many small cyclones operate in parallel achieving removal efficiencies similar or superior to high efficiency cyclones (cf. [6]). Application of cyclones as a pre-cleaner to remove abrasive particles may increase the lifetime of other abatement equipment. Cyclones are also used to recover recycling products, process materials etc. from the flue gas, e.g. in the ferrous and non-ferrous metals industry. Advantages of cyclones are: low investments, low operating and maintenance costs relative to the amount of PM removed, temperature and pressure range only limited by material, collection of dry material, relatively small in size. Disadvantages include low removal efficiencies for fine PM (or alternatively high pressure drops) and non-applicability for sticky materials. The efficiency of cyclones on BC can be assumed similar to the efficiency obtained on PM<sub>2.5</sub>,
- electrostatic precipitator (ESP): The principle behind ESP is that particles of the flue gas stream are electrostatically charged when passing through a region with gaseous ions (corona) generated by electrodes at high voltage (around 20 to 100 kV). The charged particles are then redirected in an electric field and settle at the collector walls. As large particles absorb more ions than smaller ones, ESP removal efficiency is higher for larger particles. New ESP typically may achieve PM removal efficiencies of 99% to about 99.99% if perfectly dimensioned and in optimal operation conditions, in the range 0.01 to >100 µm, older ones 90 to 99.9% [1], [7], [8]. The minimum particle size removed by ESP is <1 µm [1]. Removal efficiencies are lowest for particles with a diameter of 0.1 to 1 µm. Efficiency depends on the ESP size (collection area) but also on dust resistivity, temperature, chemical composition of the dust and gas and particle size distribution. The electrical conductivity of dust is one of the most relevant properties for ESP operation. In good and steady combustion conditions, particles are mainly composed of inorganic compounds such as salts which present ideal conductivity and are removed efficiently with the ESP. Soot and BC reveal high conductivity thus enabling high precipitation efficiency but severe re-entrainment of agglomerated particles. Condensable organic compounds (COC) from wood combustion (which are formed at low temperature from wood pyrolysis with characteristic compounds depending on residence time, heating rate, temperature and other operation parameters and at moderate temperatures and local lack of oxygen) exhibit low conductivity thus leading to back-corona which limits ESP operation [29], [30].

Dust at the collectors can be removed either dry or wet by a spray of usually water (dry or wet ESP). Dry ESPs are more common as dry collected dust is easier to handle than slurry which requires after treatment. Wet ESPs need noncorrosive materials. However, removal of particles with extremely low or high resistivity is difficult in dry ESPs whereas wet ESPs can also collect particles with high resistivity as well as sticky particles, mists or explosive dusts. Wet ESPs show also higher efficiencies for smaller particles. Injection of conditioning gases, liquids or solids, in particular water and SO<sub>3</sub>, may improve removal efficiencies [1]. Advantages of ESPs are in general very low pressure drops, very good removal efficiencies (but less pronounced for fine particles), low operating costs as well as wide applicability (sticky, glowing, high resistivity (wet ESP) particles, mists, acids, ammonia, exploding gases (wet ESP)) [1], [7], [8]. Disadvantages are high investments, high space demand, ozone formation due to high voltage, need for specialised personnel for high voltage, and limited applicability in case of varying flue gas conditions (flow rate, temperature, dust load, composition of dust) as well as necessary after treatment of slurry (wet ESPs), but almost closed water loops are achievable [1], [7], [8].

For combustion installations, ESPs can guarantee low dust and BC emissions when stable and good combustion conditions are achieved. On contrary, during transient conditions, dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and black carbon) emissions can be increased not only due to increased

raw gas concentrations, but additionally due to reduced precipitation efficiency. <u>All measures to</u> insure steady state running of combustion installations are unavoidable even if an ESP is present (refer to chapter 6.4 for optimisation of the combustion).

To achieve high efficiency of dust and BC removal with ESP, the following recommendations are provided by references [29], [30] for biomass combustion:

1. Optimum design and system integration of combustion and ESP enabling steady operation,

2. Process integrated control of ESP with specific information as indicators for the particle properties: flue gas temperature (as often carried our presently), excess air ratio, combustion temperature, water content of the fuel. This increases the range of conditions when the ESP is effective.

3. Measures to avoid re-entrainment: limitation of gas velocity to < 1.5 m/s, optimised shape of collecting plates, shorter dedusting interval during re-entrainment regimes.

The lower efficiency of ESPs on sub micrometer particles can be addressed by the use of an association of an ESP and a FF or the use of an agglomerator (see here after). These two techniques have been defined as emerging techniques by EGTEI [31].

- fabric filter (FF): In a FF the flue gasses pass through a permeable fabric where larger particles are sieved or adsorbed. The filter cake made up of collected particles supports the collection of further particles. As pressure drop increases with filter cake thickness the fabric filter needs to be cleaned from time to time. Three main cleaning mechanisms are applied: pulse jet filters where filters are cleaned by a pulse of pressurized air from the other side, shaker mechanisms and reverse gas flow. Pulse jet filters are today the most common type as they demand less space, are less expensive and applicable for high dust loadings and cause constant pressure drop [1], [9], [10]. Removal efficiencies are 99 to 99.99% for new and 95 to 99.9% for older installations [1], [9], [10] and depend on filtration velocity, particle and fabrice characteristics and applied cleaning mechanism. FF is in particular able to remove fine and ultrafine dust and is consequently efficient to remove BC. Flue gas conditioning using mainly elemental sulphur, ammonia and SO3 is applied to achieve higher removal rates, reduce pressure drop, and reduce re-entrainment of particles [1]. New developments are the addition of activated carbon or lime to achieve reactions in the filter cake as well as a catalytic filter material [1]. Flue gas temperature depends on the filter material used and the dew point of the flue gas and is in general between 120-180°C [1]. Advantages of FF are very low emission levels even down to ultrafine particles (depending on fabric) and achieved independent from dust loading, flow rate (e.g. start-ups) and dust type (----(except COC due to their sticky properties [30]), simple operation and in general no corrosion problems. Disadvantages are relatively high maintenance and operating costs due to replacement of filter bags (lifetime depends on temperature and dust) and pressure drop and in particular limitations in applicability in moist environments and for hygroscopic, glowing and sticky particles as well as for acids and ammonia and exploding gases [1], [9], [10]. Large particles need to be removed in advance [1]. Bypassing is necessary during failure.
- wet scrubber: Injecting water into the flue gas stream leads to formation of water droplets which with dust, forms a slurry. Scrubbers are mainly used for SOx removal but reduce also dust. Removal efficiencies are up to 80% for spray towers as well as dynamic and collision scrubbers and up to 99 % for venturi scrubbers [1]. The minimum particle size removed by spray towers is >10 µm, by dynamic and collision scrubbers > 2.5 µm and by venturi scrubbers >0.5 µm. Advantages of wet scrubbers are simultaneous removal of SOx and dust (and even other pollutants like HCI and HF), low maintenance, rather high removal efficiencies (in particular venturi scrubbers), few application limits (flow rate fluctuations, hot or cold, wet and corrosive gases, mists are uncritical) and reduced explosion risks from dust. Disadvantages are waste generation (slurry), high maintenance costs due to potentially high pressure drop, corrosion problems and rather low removal efficiency for very fine particles such as those to which BC is associated [1].
- oxidation techniques (described in chapter 5.3.2) used to abate VOC, PAH and odours can also be a useful technique to break down organic matter, including BC in some specific applications. Organic matter like BC can be incinerated indeed. This oxidation takes place in a thermal oxidation step in an off-gas burner, or in a catalytic oxidation installation. Oxidation techniques are used to abate anode plant emissions which partially consist of pitch and tar fumes and are rich in PAHs. Oxidation techniques abate pitch and tar fumes as well as condensed and volatile PAHs as well [32], [33].

### promising emerging dust control techniques include [31]:

- COHPAC<sup>™</sup> and TOXECON<sup>™</sup> technologies: COHPAC<sup>™</sup> (Compact Hybrid Particulate Collector) and TOXECON<sup>™</sup> are multi multi-pollutant control technologies for mercury, dioxins but also other pollutants including fine particles developed and applied in the U.S.A. In COHPAC<sup>™</sup> a FF is installed downstream of an existing ESP. As the ESP removes most of the dust, the filtration rate of the FF can be increased substantially while keeping a modest pressure drop [11]. ESP might also lead to agglomeration of very fine particles which can be then removed in the FF. TOXECON<sup>™</sup> refers to the injection of a dry sorbent like activated carbon between the ESP and FF.
- indigo Agglomerator: The Indigo Agglomerator forms large agglomerated particles by attaching fine particles to larger particles. The agglomerated particles can be easily removed using standard techniques like ESP. This technique allows also the reduction of mercury emissions [12] and may be used in case of significant concentrations of BC associated to sub micrometer particles [19].

To sum up, a variety of measures to reduce dust emissions exist. Some like cyclones are able to reduce the large and to some extent also the coarse fraction but are considerably less efficient for the fine fraction of dust. For fine and submicron dust fabric filters achieve very high removal efficiencies (up to 99.99% and above). Highly efficient ESPs, in particular Wet ESPs, as well as Venturi scrubbers may also achieve relatively high removal efficiencies for this size class up to 95% to 99%. Emerging techniques like the Indigo Agglomerator might contribute to increase ESP efficiency for fine particles by increasing the particle size.

However, when comparing removal efficiencies it need to be taken into account the characteristics of the dust and the flue gas as well as other parameters like dust load, flow rate, fluctuations as these factors may have a large impact on overall and size-specific removal performance. Furthermore removal rates largely depend on the specific design of the dust collector, e.g. on chosen filter material and ESP dimensioning, and in the end investment and operating costs.

			Removal efficiencies [%]						
	Туре		submicron fine		coarse			large	
Category		Subtype	<1 µm	0-2.5 µm		2.5-6 µm	6-10 µm	2.5-10 µm	>10 µm
			RAINS*	US EPA**	RAINS**	US E	PA**	RAINS**	RAINS*
		high efficiency		3.6		5	6		
Gravity	Gravity collector	medium efficieny		2.9		4	4.8		
and		low efficiency		1.5		3.2	3.7		
centrifugal		high efficiency		80		95	95		
collector	Centrifugal collector	medium efficieny		50		75	85		
		low efficiency		10		35	50		
	Single cyclone			10		35	50		
	Multiple cyclone without fly ash			80		95	95		
	reinjection			80		90	95		
-	Multiple cyclone with fly ash			50		75	85		
	reinjection			50		75	65		
	Cyclone/Multcyclone unspecified		11		30			70	90
	Wet cyclonic separator			50		75	85		
	ESP	high efficiency	98.6	95	99	99	99.5	99.9	99.95
	ESP	medium efficiency (unspecified)	95.4		96			99	99,9
	ESP	low efficiency (unspecified)	91.96		93			95	97
ESP	wet ESP	(1 1 1 1 1 1 )	98.86		99			99.9	99.95
		medium efficieny		50		80	94		
	ESP: boilers	low efficiency		40		70	90		
		medium efficieny		80		90	97		
	ESP: other than boilers	low efficiency		70		80	90		
		high temperature		99		99.5	99.5		
Fabric	Fabric filter	medium temperature		99		99.5	99.5		
Filter		low temperature	99.99	99	99	99.5	99.5	99.9	99.98
	Spray tower			20		80	90		
		high efficiency	95	90	96	95	99	99	99.5
Scrubber	Wet scrubber	medium efficieny		25		85	95		
		low efficiency		20		80	90		
	Venturi scrubber			90		95	99		
	Process enclosed			1.5		3.2	3.7		
	Dust suppression by water sprays			40		65	90		
	Dust suppression by chemical								
	stabilizer or wetting agents			40		65	90		
Other	Water curtain	1		10		45	90		
	Good practice: industrial processes (fugitive)	stage 1	20		10			15	20
	Good practice: industrial processes (fugitive)	stage 2	65.33		30			50	7

Table 8: Removal efficiencies of dust abatement measures for different particles size for boiler plants

Kupiainen, K. & Z. Klimont (2004) Primary emissions of submicron and carbonaceous particles in Europe and the potential for their control. - IIASA Interim Report IR-04-079, 122 pp.
\*\* Klimont, Z. J. Cofala, I. Bertok, M. Amann, C. Heyes & F. Gyarfas (2002): Modelling Particulate Emissions in Europe. - IIASA Interim Report IR-02-076, 179 pp.
\*\* US EPA (1996): AP 42, Volume I, Fifth Edition, Appendix B.2 Generalized Particle Size Distributions

Because most BC is within the fine or submicron size categories, the removal efficiencies for fine and especially submicron particles indicated in table 8 can be used as a rough proxy for BC removal efficiencies.

The selection of the most suitable measure depends on many factors related to e.g. such as the following ones:

- flue gas characteristics (dust concentration and characteristics like particle size distribution, resistivity, temperature, humidity, other pollutants present like acids, SOx, etc.),
- flow rate and fluctuations of flue gas,
- operation mode of installation,
- process specifics in industrial processes,
- new installation or retrofitting, e.g. available space,
- emission levels to be achieved,
- side and cross media effects,
- operational safety and reliability,
- site specifics,
- costs.

## 6.6 Costs of dust emission reduction techniques

Costs are an important issue when selecting PM emission reduction techniques. The following expenses may be relevant [13]:

- imputed depreciation allowance and imputed interest,
- labour costs,
- expenses for auxiliary and operating materials,
- energy costs,
- maintenance and repair costs, expenditure on monitoring, expenses for external services,
- taxes, environmental levies (e.g. charges for waste water), fees, public charges.

Costs increase in general less than the capacity of the reduction technique so that larger units are often more cost-effective. Retrofitting of existing installations is often possible but in general at higher costs.

For ESP investments are relatively high whereas maintenance and operating costs are relatively low, in particular as a result of the low pressure drop. Other costs are related to personnel specialised for high voltage and in case of wet ESP costs for slurry treatment.

For fabric filters, investments are lower but maintenance and operating costs are higher as fabrics have to be changed regularly (depending on flue gas and dust characteristics) and as the pressure drop is modest to high.

## 6.7 Side effects

Side effects of emission abatement options/techniques can be positive or negative and should be accounted for. Side effects can generally be limited by properly designing and operating the facilities. Side effects include:

- impacts on energy consumption and hence greenhouse gas emissions,
- impacts on other air pollutants,
- impacts on the use of natural resources,
- cross-media effects, e.g. on waste or water.

A core side effect of dust emission reduction is the simultaneous reduction of heavy metals (except for mercury) [14]. Depending on its characteristics and chemical composition collected dust can be recycled, e.g. in iron and steel industry, or has to be disposed.

More specifically, the side effects to be considered with different PM emission reduction techniques are:

**Electrostatic precipitator (ESP):** For ESPs a main side effect is electricity consumption for producing the corona and the electric field. However, as pressure drop is low in ESPs, overall electricity consumption is considerably lower than in FF where high pressure drops have to be compensated for. In wet ESPs treatment of the slurry is necessary but water recirculation reaches almost 100% so that waste consumption is low. As ESPs have considerably lower removal efficiencies in the size range 0.1 to 1 µm removal of heavy metals in ESPs is far lower than in FF.

**Fabric filters (FF):** Fabrics have to be changed around every 2 to 4 years (lifetime depends on various factors) so that waste is generated if reprocessing of the fabrics is not possible. The pressure drop in FFs has to be compensated for by pumping leading to additional electricity consumption. As FFs are also very effective in removal of fine particles, they also effectively reduce emissions of heavy metals which are enriched in the sub-micrometer size range of dust in flue gases.

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# 7 Available techniques for different activities

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# 7.1 Combustion installations < 1 MW with domestic combustion installations included

## 7.1.1 Coverage

Domestic combustion can be a significant source of NO<sub>X</sub>, SO<sub>2</sub>, VOCs and dust emissions (including PM<sub>10</sub>, PM<sub>2.5</sub> and black carbon (BC)) depending on the type of fuel used. This chapter covers domestic appliances used for home heating and sanitary water heating. It covers installations with a thermal input < 1 MW.

### 7.1.2 Combustion technologies

Domestic combustion appliances can be fed with different fuels, such as: natural gas, fuel oil, wood and coal. A combination of different technologies of burners and different technologies of boilers can be used in these appliances. For wood and coal use, stoves, inserts and open fire places can be used as domestic appliances, as well as manually and automatically fuelled boilers.

### 7.1.2.1 Burner technologies

### Gaseous fuels

Gaseous fuel burners are atomizing burners. Atomization increases the surface contact between air combustion and fuel; it thus improves the combustion process. Atmospheric burners are used as well as forced air burners.

Gaseous fuel burners can have different operating modes: on-off, 2 loads, modulating load.

On-off burners operate at nominal load.

2 load burners operate at nominal load or 40 - 60 % load depending on the demand.

Graduated load burners operate gradually depending on the demand, with a minimum of 30% load. This last operating mode permits a better management of the fuel consumption. Hence, emissions are reduced, especially start-up and shut-down-emissions.[1][4]

Different technologies of gaseous fuel burners can be used in domestic appliances.

**Low NO<sub>x</sub> burners** limit the formation of NO<sub>x</sub> emissions. One of the techniques used consists in recycling combustion flue gases into the burner air inlet. This reduces flame temperature, the oxygen concentration and thus enables the reduction of NO<sub>x</sub> emissions.

**Premixing type burners** mix gaseous fuel and air inside a premixing chamber. The mix is then distributed on a specific surface where the flame is developing. Different design of surface can be used. This technique enables control and optimisation of the mixing. It is based on a modular air/fuel ratio. It avoids air excess during the combustion and thus  $NO_x$  emissions. This technique can be used with catalytic combustion.

**Radiating burners** are only used with gaseous fuel. This technique permits flame temperature reduction and thus limits NO<sub>x</sub> emissions during the combustion.

## Liquid fuels

**Liquid fuel burners** are mostly atomizing burners and have the same operating modes as gaseous fuel burners: on-off; 2 loads; modulating load.

Different technologies of liquid fuel burners can be used in domestic appliances.

**Vaporizing burners** are burners where liquid fuel is atomized under gaseous form. It enables a more complete combustion and thus limits pollutant emissions but it is rarely used in boilers.

Low NO<sub>x</sub> burners are also used for liquid fuel, based on similar techniques as for gaseous fuel.

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### **Biomass fuels**

**For wood combustion**, burners are essentially used for pellets combustion in boilers or stoves. Pellets are automatically supplied to the burner with a screw conveyor.

### 7.1.2.2 Boiler technologies used with gaseous and liquid fuels

A **liquid or gas boiler** generally consists of a burner, a combustion chamber and a heat exchanger. It is equipped with a stack.

Burner burns fuel in the combustion chamber where combustion gases heat water in the heat exchanger before exiting through the stack. The heated water can be used for home heating and/or sanitary water.

Different types of boilers technologies can be used.

In **low temperature boilers**, burners are not operating at nominal load and water is heated at lower temperatures (25-75°C instead of 70-80°C). Fuel consumption reductions of 12 to 15 % can be expected in using this technology compared to the use of traditional technologies.[1][1]

**Condensing technology** is used with gaseous fuel and, increasingly, with liquid fuels. It consists in recovering the latent heat from water contained in the flue gas.

In using the heat exchanger with water at low temperature, the latent heat of the combustion gases can be recovered. Combustion gases are condensed during the heat exchange. Thus, in using condensing technology, more heat is recovered with less energy spent than using traditional technology.

Boiler yield can be increased by 15 to 20 % using this technology compared to the use of recent standard boilers.[1][1]

The firm Ökofon uses condensing technology in one of its models to diffuse the emitted dust in the condensed water contained in combustion gases. The advantage of this technique is both improvement of energy efficiency and reduction of dust emissions (-10%). However, atmospheric dust emissions avoided are contained in condensates. [8]

Flue gases from liquid fuel combustion contain less water to be condensed. Hence, condensing boiler is less used for liquid fuels.

Condensing boilers are generally associated with low NO<sub>x</sub> burners.

**Micro combustion technology** is composed of an immersed combustion chamber, and a multitubular heat exchanger. The combustion happens under the form of micro combustions (115 per second). This technology enables to recover the latent heat from water contained in the flue gas like condensing technology.

While condensing technology can be used with different type of fuel, micro combustion technology can only be used with gaseous fuel.[5][5]

### 7.1.2.3 Technologies used with biomass fuels

### Boilers

There are different types of wood boilers; mainly log boilers and pellet boilers.

Wood chip boilers can be used but are mainly used in larger installations (thermal output >30 kW).

The same technology is employed for pellet and wood chip boilers: fuel is automatically burnt by a burner and the flue gases heat a calorific fluid (generally water) in a heat exchanger.

For log wood boilers, logs are loaded on a grate and are burnt using different technologies: vertical, horizontal or inverted combustion and natural or forced draft.

For natural draft, three combustion techniques are used:

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- vertical combustion: all the wood logs loaded on the grate catch fire at the same time. This type
  of combustion is very difficult to control; hence emissions are high and energy efficiency is low
  (10-20%).
- horizontal combustion: wood logs don't catch fire at the same time. Wood logs are first dried and then burnt. Flames are horizontal. This type of combustion is easier to control than horizontal combustion and thus performances are higher.
- inverted combustion: as in horizontal combustion, wood logs don't catch fire at the same time and are dried before being burnt. It is called inverted combustion because instead of going up as in vertical combustion, flames are going down, through the grate. It is the best controlled combustion type for natural draft; hence performances are the highest.

Forced draft boilers (also called "turbo" boilers) are more recent and have higher performances than natural draft. Technique employed is the same as inverted combustion, but in "turbo" boilers, introduction of combustion air is made by a fan and flue gases are sucked out. These types of boilers apply staged combustion. Here primary air introduced on top of the fuel is involved in drying the wood and in a gasification process which occurs in the first stage. In the second stage, gas combustion is activated by the injection of secondary air. <u>Staged combustion and gasification in the fuel bed [15]</u>. The control of combustion is improved thus enabling high efficiency and high temperature, key factors for a <u>complete combustion</u>, and <u>T</u>these boilers have higher the highest performances.

In log wood boilers, a heat storage tank can be used to avoid part-load operating conditions. The boiler can be operated at full load or at steady-state part-load which reduces emissions of combustion residues. In manually or automatically operated boiler, a heat storage tank is advisable as it helps to reduce part load emissions.

Low NO<sub>x</sub> technology as recycling of the combustion flue gases can also be applied to wood boiler. Self cleaning option is available for some boilers. It contributes to maintain appliances energy efficiency.

### Other domestic appliances

Stoves, inserts and open fire places can be used for wood combustion:

- open fireplaces are the worst technique: combustion is made in the ambient air. There is no control of the combustion, energy efficiency is bad and emissions are high.
- different technologies can be used in inserts: air regulation (air combustion can be heated before to be injected in the combustion chamber), catalysis (a catalyst is added to drop combustion temperature).
- stoves: different technologies can be used.
  - air regulation: air combustion can be heated before being injected in the combustion chamber and it can be controlled automatically using an electronic device. This option reduces real-life emissions.
  - fuel used (pellets or wood logs) varies from a technology to another. Masonry stove can
    accumulate energy during the combustion and then diffuse heat several hours after
    combustion.
  - airtight stove: outside air is used as air combustion. There is thus no air exchange between combustion air and inside air. Performances of this technique are higher than a classic stove and it avoids indoor air quality problems.

Energy efficiency of appliances depends a lot on heat exchange. Therefore, improvements in heat exchange are always in development. Longer smoke pipe and the use of fan for convection air can be used. It transfers more energy from flue gases to indoor air and thus improves energy efficiency and reduces emissions.

Appliances performances depend also on combustion rateload. When the rate of combustionload is lower than the nominal rate-load (reduced combustion), combustion is bad; emissions are higher and energy efficiency is lower. This is due to the low temperature in the combustion chamber.

Automatic appliances, which burn pellets or wood chips, enable to operate at a nominal combustion rate; therefore <u>better</u> performances are <u>obtained better</u> and <u>dust</u> emissions<u> as well other unburnt</u> <u>pollutants due to incomplete combustion such as CO and VOCs</u> are lower than with manual appliances.

### 7.1.2.4 Technologies used with solid fossil fuels

No information is available at the moment concerning technologies using coal.

### 7.1.3 Available Techniques, Emission Levels

Reducing emissions in domestic combustion mainly means increasing appliances energy efficiency by using advanced technologies. Nevertheless, so as to achieve the best energy efficiency, measures taken on appliances have to be followed through by measures on buildings thermal insulation and on the whole heating network.

Pollutant emissions depend on the type of fuel used:

- gaseous fuels use is mainly a source of NO<sub>X</sub> emissions.
- liquid fuels use is mainly a source of SO<sub>2</sub> and NO<sub>X</sub> emissions.
- solid fuels: emissions arising from wood combustion are mainly dust and VOC while emissions from coal combustion are mainly SO<sub>2</sub> and dust.

Combustion technologies depend also on the type of fuels used. Therefore, available techniques to reduce emissions from domestic appliances mainly depend on it too.

## 7.1.3.1 Type of fuel used

### Gaseous fuels

Condensing boiler technology combined with the use of a specific burner can be considered as high efficient technique when gaseous fuels are used. Specific burners enable further reduction especially low  $NO_x$  burners for  $NO_x$  emissions. Micro combustion can also be considered as high efficient technique with the use of gaseous fuels. [1][4][2][2].

### Liquid fuels

Low temperature or condensing boilers combined with the use of specific burners are considered as high efficient technique with the use of liquid fuels. Further  $NO_x$  emission reductions can also be achieved by the use of specific burners.

### **Biomass fuels**

For wood logs boilers, inverted combustion with forced draft and recycling of the combustion flue gases can be considered as high efficient technique. Energy efficiency can be increased and emissions reduced with the use of a water tank as hydro-accumulator.

The use of pellets as fuel in boilers can also be considered as high efficient technique, so is the use of condensing technology for solid fuels use.

Dust and VOC emission level mainly depend on the combustion efficiency; the more complete the combustion is, the lower are the emission levels.

For inserts, the use of catalysts reduces atmospheric emissions of combustion residues by dropping combustion temperature. This technique is currently used in USA and begins to appear in Europe. According to measurements reports [10][10] and [11][11], use of catalysts in inserts can divide dust emissions by two.

For stoves, the use of pellets can be considered as a high energy efficiency technique.

Masonry stoves diffuse energy stored during several hours. It allows obtaining a good ambient temperature during several hours without use reduced combustion which produces a lot of pollutants.

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However, any technology used to increase energy saving and combustion efficiency, whatever fuel used, contributes to pollutant emissions reduction by reduction of fuel consumption.

## Solid fossil fuels

No information is <u>was</u> available at the moment concerning technologies using coal when the guidance was drafted.

### 7.1.3.2 Pollutants

### SO<sub>2</sub>

 $SO_2$  emissions depend on the sulphur content of the fuel used. Therefore, the main measure to reduce  $SO_2$  emissions is to use sulphur-free fuels or fuels with low sulphur content. For brown coal, the addition of calcium hydroxide is possible in order to fix sulphur in the ash.

### NOx

 $NO_x$  emissions are influenced by different parameters such as: the type of fuel, the flame temperature, the air volume, the residence time in the combustion chamber and the nitrogen content of the fuel.

Available techniques to reduce specifically  $NO_x$  emissions are the use low  $NO_x$  burners or premixed modular air/fuel ratio burner. The premixed modular air/fuel ratio burner enables the  $NO_x$  formation reduction in controlling the air content in the mix.

The following table gives an overview of achievable  $NO_x$  emission levels using selected gas firing domestic combustion appliances at full load.

# Table 1: achievable NO<sub>x</sub> emissions using selected gas firing domestic combustion appliances. [2][2]

	Heat output (kW)	NO <sub>x</sub> (g/GJ)
Forced air condensing boiler + premixing burner with modular gas/air ratio	24	18
Forced air boiler + premixed low-NO <sub>x</sub> burner	24	29
Forced air boiler + conventional burner	24.6	62
Conventional boiler and burner	24.2	85

## VOCs

VOC emissions are mainly influenced by the combustion efficiency. There is no technology used to reduce specifically VOC. Available techniques to reduce VOC emissions are actually the use of technologies enabling the most complete combustion as possible. These technologies are detailed in the previous paragraphs concerning wood fuel technologies.

### Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

In domestic combustion as in combustion in general, dust emissions are influenced by the type of fuel used. With the use of <u>gG</u>aseous <u>fuels have very low dust emissions are considerably lew-and gas-can</u> <u>be used to substitute coal and/or wood.</u> <u>or For57</u> liquid fuels, <u>dust emission are also low.</u> <u>measures to</u> <u>improve energy efficiency are primary Primary</u> measures to reduce dust emissions are presented in chapter 7.1.2.1 and 7.1.2.2. They are the only measures considered in this chapter to reduce dust emission from gaseous or liquid fuels use.

Solid fuels are the main source of dust emissions. Available techniques to reduce dust emissions are foremost primary measures enabling the most complete combustion as possible. These techniques

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have been described in the previous paragraphs concerning wood fuel technologies. Dust emissions from existing appliances can be obtained by replacing them with modern appliances showing higher energy efficiency and better combustion conditions.

Besides those technical measures, especially for manually operated wood stoves and boilers, proper operation and quality of fuel are essential to avoid high-pollutant emissions in practice. Ignition of the wood from the top instead of ignition from the bottom significantly reduces emissions from the start-up phase. Throttling the combustion air leading to low heat loads needs to be strictly avoided- [15]. The use of untreated wood only and the correct seasoning of wood for moisture content are also very important prerequisites. Public information programs can help in raising the awareness for these requirements [16].

Secondary measures to reduce dust emissions can also be considered with the use of solid fuels. The proven technologies for dust removal are multicyclones, electrostatic precipitators (ESP) and fabric filters which are described in more detail in paragraphs 6.5 and 7.1.2.3.

Studies have shown that ESP and fabric filters are suited in the range <1 MW down to 100 kW [8][4]. For installations < 500 kW, costs are still relatively high, but there is positive experience with some reference installations in this range. Dust emission reductions below 50 mg/m<sup>3</sup> (13% O<sub>2</sub>) can be reached with a simple (1-stage) ESP, while reductions to 10-20 mg/m<sup>3</sup> (13% O<sub>2</sub>) have been demonstrated with optimized (multi-stage) ESP. Fabric filters can reduce dust emissions to < 10 or even <5 mg/m<sup>3</sup> [8][6]\_ [15].

Small-scale electrostatic precipitators (ESP) have been developed in some countries, e.g. Norway, Germany and Switzerland [18] [13], [17], and can be considered as available techniques to reduce dust emissions from domestic wood combustion appliances < 50 kW including single-room heaters. Under ideal conditions small-scale ESP can reduce 90 % of the dust particles with a diameter superior

to 0.1 µm [7][7]. However these separators are often based on a design which for cost reasons is simplified compared to industrial applications. In some cases only moderate separation efficiencies below 50% may be expected, especially when there is re-entrainment after agglomeration of particles. Field tests have shown that small-scale ESP now available on the market are only effective on the long-term when used with modern combustion installations enabling a rather complete and clean combustion. Older combustion installations with poor combustion technology and correspondingly high particulate emissions may quickly lead to overload and clogging [8][48]. In the current state of the art a

general retrofitting of older installations with small-scale ESP is not recommended.

More generally, dust is deposited in the stoves, boilers, ducts, stacks, etc. Thus, to limit emissions of dust, boilers or stoves need to be cleaned regularly. Self cleaning option can also be seen as an efficient technique for the dust reduction.

### Table 2: achievable dust emission levels of biomass combustion appliances < 1 MW [2][16]

Appliance type	<ol> <li>Secondary abatement technology</li> </ol>	<ul> <li>Achievable dust emission level</li> <li>mg/mn<sup>3</sup> at 13% O<sub>2</sub></li> </ul>
Wood stoves and closed insert appliances		20 - 40
Log wood boilers (with heat storage tank)		15 -30
Pellet stoves & boilers		15 - 30
Automatic wood	multicyclone	75 - 150
boilers	simple ESP	20 - 50
	improved ESP	< 10 - 20
	fabric filter	< 10

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### Focus on black Carbon (BC)

Residential combustion - especially biomass combustion - is and remains in the future a key BC emitting sector. Soot (found as BC in the atmosphere) is formed under conditions of incomplete combustion in zones of high temperatures and lack of oxygen. Incomplete combustion is often found in manually operated combustion. Hence manually operated wood stoves and small-size boilers are the main BC sources in this source category.

Available techniques to reduce BC emissions are the same technical primary measures as described above for dust reduction by enabling the most complete combustion as possible. Especially staged combustion comprising lower temperature gasification will reduce soot formation by reducing fuel rich, high temperature zones in the flame. Again - as for dust reduction - proper operation of manually operated appliances and quality of fuel are also essential for BC reduction [15].

In automatic combustion installations - automatic wood boilers, pellet stoves and boilers - nearly complete combustion can be achieved and hence inorganic particles are dominant as dust components. However, during start-up, and in phases of inappropriate operation, soot can also be emitted from automatic installations [15].

Concerning secondary measures, in general electrostatic precipitators (ESP) and fabric filters will reduce BC. Soot has a high electrical conductivity thus enabling high separation efficiency in ESPs-but severe re entrainment of agglemerated particles can occur. Multicyclones will not reduce BC to any significant degree, since they have a poor separation efficiency for particles smaller than 5 microns [15].

For small-scale ESPs marketed for use with domestic stoves and boilers, the BC reduction potential in practice is uncertain for most applications and hence further experience is needed [8][18].

### 7.1.4 Emerging techniques

The micro-cogeneration is an emerging technique to reduce energy consumption. The energy use for home heating or sanitary water heating is also used to produce electricity.

The use of pellets which is being developed for inserts technology increases energy efficiency.

Ceramic filters have been used for large industrial installations over longer periods. For small combustion installations, ceramic filters have been developed that use the same technology as particle traps for diesel engines in vehicles and vessels. These soot filters also reduce emissions of BC. Ceramic filters can also be used in oxidation installations. The ceramic material transfers the heat for the oxidation reaction or functions as a catalyst. This way unburned material like BC can be oxidised. These emission abatement systems have been developed and tested in practice but not enough data are available to assess the availability for stationary combustion plants < 1 MW. It is expected that the development of this abatement technique will benefit from the use of particle traps on heavy duty vehicles and that this will become an available technique for small combustion plants burning solid fuels in the near future [19].

### 7.1.5 Cost data for emission reduction technique

The investment cost of a low-NO<sub>x</sub> boiler is about 500 euros more than for a conventional boiler 10[10].

The investment cost for a wood boiler with inverted combustion and forced draft is from 3 000 to 7 650 euros, for installations from 15kW to 150kW. An investment for heat accumulator is from 1 500 to 2 750 euros [10][40], [12][42].

The investment cost for a pellet boiler is 7 000 to 15 000 euros for installations from 15 kW to  $\frac{12}{12}$ .

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Guidance document on control techniques for emissions of sulphur, NOx, VOCs and dust (including $\rm PM_{10},PM_{2.5}$ and black carbon) from stationary sources	
According to Swiss studies [13][13], the investment cost for a small-scale ESP reducing at least 60 %	Code de champ
of dust emissions would be 1 000 to 1 500 euros for installations $< 35$ kW.	 Mis en forme :

Additional cost of catalysts addition in inserts is about 1 000 euros [14][14].

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Table 2: investment per kW heat output for wood heating systems and dust abatement equipment [8][8]<sup>1</sup>

Power [kW]	Technology (heater system) [€/kW]	Building (without silo) [€/kW]	ESP [€/kW]	FF [€/kW]
				• •
100	965	520	660	450
200	800	430	405	240
500	630	340	195	115
1000	420	225	115	70
2000	315	170	75	50

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<sup>1</sup> Data from 2005/2006, converted to € (1 SFR= 0,64523 €) and rounded ; for calculation details see source report

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## 7.2 Combustion Installation from 1 to 50 MW

## 7.2.1 Coverage

This section covers emissions from boiler installations and gas turbines with a net thermal input between 1 and 50  $MW_{th}$ . In the following, the term "boilers" is meant in contrast to combustion engines or turbines and includes all kinds of boilers and process heaters.

The following installations are not covered by this section:

- plant in which the products of combustion are used for direct heating, drying, or any other treatment of objects or materials, e.g. reheating furnaces, furnaces for heat treatment;
- post-combustion plant, i.e. any technical apparatus designed to purify the waste gases by combustion that is not operated as an independent combustion plant;
- facilities for the regeneration of catalytic cracking catalysts;
- facilities for the conversion of hydrogen sulphide into sulphur;
- reactors used in the chemical industry;
- coke battery furnaces;
- cowpers;
- waste incinerators;

and

 plant powered by diesel, petrol or gas engines, irrespective of the fuel used (For information about stationary engines see document "New stationary Engines" 7-41)

## 7.2.2 Combustion technologies

Within the sector, the technologies used for the combustion of liquid and gaseous fuels are similar to those for production of thermal energy in industrial combustion activities.

For the combustion of solid fuels and biomass mainly fixed bed combustion technology, i.e. grate-firing, is applied.

Fluidized bed combustion technologies are also used in the sector. This technology is most appropriate for co-combustion of coal with biomass and/or with waste fuels, or combustion of biomass

Gas turbines are used for the transformation of thermal energy into mechanical energy. They use a steady flow of a gas (mostly air), compressed and fired with gaseous or liquid fuel.

## 7.2.3 Available Techniques, Associated Emission Levels (AEL)

Emissions within the sector strongly depend on the fuel, combustion technologies as well as on operational practices and maintenance. For solid fuels specific emissions are higher in smaller than in larger plants. For gaseous and liquid fuels, the emissions are not significantly higher in comparison to industrial scale boilers due to the quality of fuels and design of burners [4],[1]

## 7.2.3.1 SO<sub>2</sub>

Table 1: emission sources and selected  $SO_2$  control measures with associated range of emission levels (solid and liquid fuels) resp. upper emission level (gaseous fuels) in combustion installations between 1 and  $50MW_{th}$ [1]

Emission source	Control measures	Control measures SO <sub>2</sub> emission level (mg/Nm <sup>3</sup> )				
Solid fuel						
	Use of low-sulphur fuel,					
Boilers other than fluidized bed combustion (FBC)	Sorbent injection,	50-1000				
	Flue gas desulphurisation,					
Fluidized bed combustion	Use of low-sulphur fuel,					
	Sorbent injection,	50-400				
	Flue gas desulphurisation,					
	Liquid fuel					
Boilers	Use of low-sulphur fuel,					
	Sorbent injection,	50-850				
	Flue gas desulphurisation					
Gaseous fuel						
Boilers: Refinery gas	Use of low-sulphur fuel,	100				
Boilers: Liquefied gas	Sorbent injection,	5				
Boilers: Other gaseous fuel	Flue gas desulphurisation	35				
If not stated attaction values are delin suprame accuming an ovigen content by volume in the worst and of						

If not stated otherwise, values are daily averages assuming an oxygen content by volume in the waste gas of 3 % in the case of liquid and gaseous fuels, 6 % in the case of solid fuels.

If emission reduction measures are regarded, for low sulphur fuels a level of 700 mg/Nm<sup>3</sup> can be reached, for sorbent injection a level of  $200 - 400 \text{ mg/Nm}^3$  and for desulphurisation a level of  $50 - 200 \text{ mg/Nm}^3$ .

## 7.2.3.2 NO<sub>x</sub>

Table 2: emission sources and selected NOx control measures with associated upper emission levels in combustion installations between 1 and  $50MW_{th}$  [1], [2][1], [2]

Emission source	Control measures	NO <sub>x</sub> emission level (mg/Nm <sup>3</sup> )							
Solid fuel									
Grate firing	Low-NOx burner								
	Air staging	< 200-400							
	Flue gas recirculation	200 400							
	Boiler design								
Pulverized coal	Low-NOx burner	< 200-400							
	Air staging								
	Flue gas recirculation								
	Boiler design								
	Air staging								
	Flue gas recirculation	< 200-500							
Fluidized bed combustion	Boiler design								
	SNCR	< 50-100							
	Liquid fuel								
	Low-NOx burner								
	Air staging								
Boiler	Flue gas recirculation	< 200-300							
	Boiler design								
	Gaseous fuel								
	Low-NOx burner								
	Air staging	202							
Boiler	Flue gas recirculation	< 200							
	Boiler design								
	Existing Gas-Turbines								
	Water and steam injection or	50-120							
Fuel: natural gas	SCR	50-120							
Fuel: diesel oil or process gas	Water and steam injection or SCR								
	New Gas-Turbines	•							
Fuel: natural gas	Dry low-NO <sub>x</sub> premix burner or SCR	20-50							
	daily averages assuming an oxygen cor eous fuels, 6 % in the case of solid fuel								

### 7.2.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

Table 3: emission sources and selected dust control measures with associated range of emission levels in boiler installations between 1 and 50  $MW_{th}$ [1]

	Emission source	Control measures	Dust emission level (mg/Nm <sup>3</sup> )	
			new	existing
	Solid fuel, 1- <u>to</u> 5 <u>MWth</u>	Cyclone	< 50	< 100
		ESP	5 - 20	5 - 30
		FF	5 - 20	5 - 20
	Solid fuel, 5 - <u>to</u> 50 <u>MWth</u>	ESP	5 - 20	5 - 30
		FF	< 5 - 20	< 5 - 20
		ESP	5 - 50	5 - 50
	Liquid fuels, 1- <u>to 5 MWth</u>	FF	< 5 – 20	< 5 – 20
		Use of low ash fuel	< 5 - 50	< 5 - 50
Liquid fuels	Liquid fuels 5 to 50 MW/th	ESP	5 - 20	5 - 50
	Liquid fuels, 5 - to 50 <u>MWth</u>	FF	< 5 - 20	< 5 - 20
	Gaseous fuels		2 - 5	2 - 5

If not stated otherwise, values are daily averages at standard conditions assuming an oxygen content by volume in the waste gas of 3 % in the case of liquid and gaseous fuels, 6 % in the case of mineral solid fuels, 11 % in the case of wood

Because BC is formed during incomplete combustion. <u>I</u>, it is mainly associated to particles with a diameter less than 1 µm. <u>In such combustion installations</u>, <u>BC content of dust can increase during start-up and shut-down periods</u>. A smooth, continuous and optimised combustion reduces dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC) emissions as described in chapter 6.4. QOnly reduction techniques able to remove fine particles will have a significant efficiency on BC emissions. In such combustion installations, <u>BC content of dust can increase during start-up and shut-down periods</u>. Combustion installations, <u>BC content of dust increases during start up and shut down periods</u>. Combustion installations, <u>BC content of dust increases during start up and shut down periods</u>. Combustion technique optimisation reduces dust (including PM<sub>10</sub>, PM<sub>2.6</sub> and BC) emissions as described in chapter 6.4. Chapter 6.5 provides information on the efficiency of ESP and FF for dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC).

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## 7.3 Combustion Installations larger than 50 MW

## 7.3.1 Coverage

The combustion sector covers a range of different combustion techniques suited to different fuels: solid fuels, such as coal, lignite, peat, biomass, liquid and gaseous fuels, including low calorific and blast furnace gas. This section covers boilers (small:  $50 - 100 \text{ MW}_{th}$ , medium:  $100 - 300 \text{ MW}_{th}$ , and large: >  $300 \text{ MW}_{th}$ ) and gas turbines (>  $50 \text{ MW}_{el}$ ). In the following, the term "boilers" is meant in contrast to combustion engines or turbines and includes all kinds of boilers and process heaters. The given capacity classes in terms of rated thermal input refer to the lower heating value (LHV) of the respective fuel.

The following installations are not covered by this section:

- plant in which the products of combustion are used for direct heating, drying, or any other treatment of objects or materials, e.g. reheating furnaces, furnaces for heat treatment;
- post-combustion plant, i.e. any technical apparatus designed to purify the waste gases by combustion that is not operated as an independent combustion plant;
- facilities for the regeneration of catalytic cracking catalysts;
- facilities for the conversion of hydrogen sulphide into sulphur;
- reactors used in the chemical industry;
- coke battery furnaces;
- cowpers;
- waste incinerators;
  - and
- plant powered by diesel, petrol or gas engines, irrespective of the fuel used (For information about stationary engines see document "New stationary engines" 7-41)

## 7.3.2 Emission sources

The combustion process leads to the generation of emissions to air, which are considered to be one of the major sources of air pollution. Depending on the type of the fuels, several combustion technologies are available which show considerably different  $NO_x$ ,  $SO_x$  and dust (including  $PM_{10}$ ,  $PM_{2.5}$  and BC) emissions. This paragraph describes the main technologies used for the combustion of solid, liquid and gaseous fuels.

### (a) Large boilers, process heaters and furnaces

Grate firing is used in comparatively small combustion plants with a thermal capacity of less than 100  $MW_{th}$  sometimes grate firing is used for burning waste (not regarded in this chapter, cf. 7-18) and biomass [1]. The fuel on the grate will be first dried and pyrolysed. And then the char is burned on the grate. The conditions of combustion are not as well controlled as in other systems as the combustion chemistry and the temperature can vary considerably across the grate [2].

**Pulverised fuel firing** is well established for all sizes of boiler above 50  $MW_{th}$  and is a solid fuel burning technique in which the fuel is pulverised before being ignited. Two general boilers types are distinguished:

**Dry bottom boilers** operate at lower temperatures so that the ash is not heated above its melting point during the combustion process.

Wet bottom boilers require high combustion temperatures in order to melt the ash; accordingly, comparatively high NOx emission levels are observed [1]. This technique is often used for fuels with poor combustion characteristics and involves recycling fly ash [3].

Fluidized bed combustion (FBC) is a combustion technology for burning hard coal and lignite, but also low-grade fuels such as waste, peat and wood, which are not regarded in this section. Fuel is injected into a hot turbulent bed of reactive or inert material while a flow of air passes up through the bed. Emissions can be further reduced via integrated combustion control in the system. Within the sector of energy conversion, atmospheric fluidized bed combustion is a well-established commercial technology. Depending on the velocity of the fluidisation air, two types of atmospheric fluidised bed combustion do exist, the atmospheric bubbling fluidised bed combustion (BFBC), and the atmospheric circulating fluidised bed combustion (CFBC). Pressurized fluidized bed combustion (PFBC) operates at elevated pressures and produces a high-pressure gas stream at temperatures that can drive a gas turbine.

### (b) Turbines

**Gas turbines** are used for the transformation of thermal energy into mechanical energy. They use a steady flow of a gas (mostly air), compressed and fired with gaseous or liquid fuel. Gas turbines are increasingly used for electricity production in base and intermediate load but are also still used for peaking load in simple cycle (then fired with gas or light oil). In combined cycle power plants a gas turbine is combined with steam turbine to generate electricity.

**Integrated gasification combined cycle (IGCC)** process incorporates coal or biomass gasification and combined cycle plants. The gasified solid fuel is burned in the combustion chamber of the gas turbine. The technology also exists for heavy oil residue. However, this process is not yet fully commercialized, a small number of demonstration units, mainly around 250 MWe size are being operated in Europe and the USA.

### BAT for the combustion of solid, liquid and gaseous fuels

### Combustion of coal and lignite

Pulverized combustion, fluidized bed combustion as well as pressurized fluidized bed combustion and grate firing are all considered to be BAT for the combustion of coal and lignite for new and existing plants. Grate firing should preferably only be applied to new plants with a rated thermal input below 100 MW [3].

### Combustion of biomass and peat

For the combustion of biomass and peat, pulverized combustion, fluidized bed combustion as well as the spreader stoker grate firing technique for wood and vibrating, water-cooler grate for straw-firing are BAT. Pulverized peat combustion plants are not BAT for new plants [3].

### **Combustion of liquid fuels**

For liquid fuels, the use of pretreatment devices, such as diesel oil cleaning units used in gas turbines and engines, are BAT. Heavy fuel oil (HFO) treatment comprises devices such as electrical or steam coil type heaters, de-emulsifier dosing systems, etc.

### Combustion of liquid and gaseous fuels in CHP plants

A combined cycle operation and cogeneration of heat and power is to be considered as the first BAT option, i.e. whenever the local heat demand is great enough to warrant the construction of such a system [3].

### 7.3.3 BAT, Associated Emission Levels (AEL)

### 7.3.3.1 SO2

This section provides descriptions of the abatement options that are generally used to reduce emissions of sulphur oxides from combustion installations. Emissions of  $SO_2$  are highly dependent on the sulphur content in coal burned and the emissions control system employed. In general, techniques to reduce sulphur oxides are divided into primary and secondary measures.

### **Primary measures**

**Use of low sulphur fuel**, the SO<sub>2</sub> emissions during combustion are directly related to the sulphur content of the fuel used. Fuel switching (from high- to low-sulphur fuels) leads to lower sulphur emissions. This measure is widely applied. However there may be certain restrictions, such as the availability of low-sulphur fuels and the adaptability of existing combustion systems to different fuels. Fuel switching to natural gas can be sufficient for reducing SO<sub>2</sub>, in case of other fuels depending on the fuel sulphur content it can be used as a supplementary technique.

### Use of alkaline sorbents in fluidised bed combustion systems.

FBC boilers can operate very efficiently in terms of  $SO_2$  removal, for example sorbent injection into the FBC boiler is an inexpensive method for sulphur capture. Investment costs are low, because the desulphurisation is incorporated into the combustion process and separate reactor equipment is not needed [3]. However, the solid by-products composed of ash, sulphate containing reaction products and lime cannot be used for concrete making as fly ash from conventional PC combustion

### Secondary measures

Flue gas desulphurisation (FGD) processes. These processes aim at removing already formed sulphur oxides, and are also referred to as secondary measures. The state-of-the-art technologies for flue gas treatment are all based on the removal of sulphur by wet or dry processes.

In wet processes, wet slurry waste or by-product is produced, and flue gas leaving the absorber is saturated with moisture. Seawater scrubbing utilises seawater's inherent properties to absorb and neutralise sulphur dioxide in flue-gases. If a large amount of seawater is available near a power plant, it is most likely to be used as a cooling medium in the condensers. Wet scrubbers, especially the limestone-gypsum processes, are the leading FGD technologies. They have about 80% of the market share and are used in large utility boilers. The efficiency of sulphur dioxide removal may be increased up to 92-98%. In case of retrofitting the efficiencies are lower reaching up to 95%.

In semi-dry processes, a slurry of alkaline reagent is atomized and injected into a vessel where it reacts with the  $SO_2$  in the flue gas to produce calcium sulphate or sulphite products [4]. Sulphur dioxide removal efficiencies of 80 to 95% have been achieved.

Table 1: emission sources and selected BAT SOx control measures with associated emission
levels in combustion installations (PM is for primary measures)

Emission source	Combination of control measures	SO <sub>x</sub> emission level associated with BAT <sup>1</sup> (mg/Nm <sup>3</sup> ) [3]	
	boilers 50 - 100 MW <sub>th</sub>		
Grate-firing, Fuel: coal and lignite	Low sulphur fuel or FGD	200 - 400	
Boiler;		200 - 400	
Fuel: coal and lignite	Low sulphur fuel and FGD	(split view industry: 200 - 300)	
Circulating FBC; Pressurised	Low sulphur fuel	150 - 400	
FBC; Fuel: coal, lignite	Limestone injection	(split view industry: 150 - 300)	
Bubbling FBC;	Low sulphur fuel	150 - 400	
Fuel: coal, lignite	FGD	(split view industry: 150 - 300)	
Boiler; Fuel: peat	Limestone injection Calcium hydroxide injection in dry form before the ESP or FF FGD	200 - 300 (new) 200 - 300 (existing)	
Circulating FBC; Bubbling FBC; Fuel: peat	Co-combustion of biomass and peat Limestone injection Calcium hydroxide injection in dry form before the ESP or FF FGD	200 - 300 (new) 200 - 300 (existing)	
Boiler; Fuel: oil	Low sulphur fuel oil Co-combustion of gas and oil FGD	100-350 (new) 100-350 (existing) (split view industry: new plants: 200-850, existing plants: 200-850)	
	Boilers 100 - 300 MW <sub>th</sub>		
	Low sulphur fuel	100 - 200 (new)	
Boiler;	FGD	100 - 250 (existing)	
Fuel: coal and lignite	Combined techniques for the reduction of NOx and SOx	(split view industry: existing plants 100-600)	
Circulating FBC; Pressurised FBC; Fuel: coal, lignite	Low sulphur fuel Limestone injection	100 - 200 (new) 100 - 250 (existing) (split view industry: existing plants: 100-300)	
Bubbling FBC; Fuel: coal, lignite	Low sulphur fuel FGD	100 - 200 (new) 100 - 250 (existing) (split view industry: existing plants 100-300)	
Boiler; Fuel: peat	Limestone injection Calcium hydroxide injection in dry form before the ESP or FF FGD	200 - 300 (new) 200 - 300 (existing)	
Circulating FBC; Bubbling FBC; Fuel: peat	Co-combustion of biomass and peat Limestone injection Calcium hydroxide injection in dry form before the ESP or FF,	150 - 250 (new) 150 - 300 (existing)	

	FGD	
	Low sulphur fuel oil	
	Co-combustion of gas and oil	100 - 200 (new)
Boiler;	and FGD	100 - 250 (existing)
Fuel: oil	FGD	(split view industry: new plants:
	Combined techniques for the reduction of NOx and SOx	100-400, existing plants: 100-400)
	Boilers >300 MW <sub>th</sub>	
	Low sulphur fuel	20 - 150 (new)
	FGD	20 - 200 (existing)
Boiler; Fuel: coal and lignite		( <b>C</b> ,
	Combined techniques for the reduction of NOx and SOx	(split view industry: new plants: 20-200, existing plants: 20-400)
		100 - 200 (new)
Circulating FBC; Pressurized	Low sulphur fuel	100 - 200 (existing)
FBC, Fuel: coal, lignite	Limestone injection	(split view industry: existing plants: 100-300)
		20 - 150 (new)
Bubbling FBC, Fuel: coal, lignite	Low sulphur fuel	20 - 200 (existing)
	FGD	(split view industry: existing plants: 20-300)
	FGD	50 - 150 (pew)

Combined techniques for the

Calcium hydroxide injection in

Co-combustion of gas and oil

Combined techniques for the

reduction of NOx and SOx

dry form before the ESP or

reduction of NOx and SO<sub>2</sub> Co-combustion of biomass

Limestone injection

Low sulphur fuel oil

and peat

FF FGD

FGD

Guidance document on control techniques for emissions of sulphur, NOx, VOCs and dust (including  $PM_{10}$ ,  $PM_{2.5}$  and black carbon) from stationary sources

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

If not stated otherwise, values are daily averages assuming an oxygen content by volume in the waste gas of 3 % in the case of liquid and gaseous fuels, 6 % in the case of solid fuels.

## 7.3.3.2 NO<sub>x</sub>

Boiler; Fuel: peat

Fuel: peat

Boiler, Fuel: oil

Circulating FBC; Bubbling FBC

The most important oxides of nitrogen with respect to releases from combustion processes are nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O). NO and NO<sub>2</sub> are commonly referred to as NO<sub>x</sub>. [2]. NO<sub>x</sub> is formed during most combustion processes by one or more of three chemical mechanisms: "thermal" NO<sub>x</sub> resulting form oxidation of atmospheric molecular nitrogen, "fuel" NO<sub>x</sub> resulting from oxidation of chemically bound nitrogen in the fuel, and "prompt" NOx resulting from

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50 - 150 (new)

50 - 200 (existing)

50 - 200 (new)

50 - 200 (existing)

50 - 150 (new)

50 - 200 (existing)

(split view industry: new plants:

50-200, existing plants: 50-400)

reaction between atmospheric molecular nitrogen and hydrocarbon radicals [4]. Only the first two mechanisms are of major importance in combustion plants.

This section provides descriptions of the abatement options that are generally used to reduce emissions of nitrogen oxides from combustion installations. In general, techniques to reduce nitrogen oxides are divided into primary and secondary measures. Primary measures have been developed to reduce  $NO_x$  emissions at source during the combustion process by regulating flame characteristics such as temperature and fuel-air mixing. Secondary measures operate downstream of the combustion process and remove  $NO_x$  emissions from the flue gas.

The application of primary measures is limited by operational and fuel specific parameters that influence the safe operation. It is also limited by layout feasibility in existing installations.

### Primary measures (combustion modifications):

Air staging consists of the introduction of combustion air into primary and secondary flow sections to achieve complete burnout and to encourage the formation of  $N_2$  rather than  $NO_x$ . The primary combustion zone has a lack of oxygen and the secondary combustion zone an excess of oxygen. This technique is frequently used in conjunction with low  $NO_x$  burners, completes the combustion process at a lower temperature [1], [5].

**Fuel staging,** also named **reburning** is a three-stage (zone) system. It is based on the creation of different zones in the furnace by staged injection of fuel and air. The aim is to reduce nitrogen oxides, which have already been formed back to nitrogen [1]. The reburning technique is capable of achieving relatively high NO<sub>x</sub> reduction (50-75%) and can in principle be used at all types of fossil fuel fired boilers, and also in combination with low-NO<sub>x</sub> combustion techniques for the primary fuel. This technique is not well adapted for retrofit due to space constraints.

**Flue gas recirculation** results in a reduction of available oxygen in the combustion zone and, since it directly cools the flame, in a decrease of the flame temperature: therefore, both fuel bound nitrogen conversion and thermal NO<sub>x</sub> formation are reduced. The recirculation of flue gas into the combustion air has proven to be a successful method for NO<sub>x</sub> abatement at high temperature combustion systems such as wet bottom boilers and oil or gas fired installations but is generally not effective on dry bottom pulverised coal boilers. NO<sub>x</sub> emissions reduction of 30-60% can be observed by employing flue gas recirculation when burning natural gas. On heavy fuel oil NO<sub>x</sub> reductions of 10-20% are observed but dust emissions may increase

**Low NO<sub>x</sub> Burners (LNB)** are designed to control the mixing of fuel and air to achieve what amounts to staged combustion. An under-stoichiometric zone is created with a fuel/air mixture and primary air. Due to the swirl of primary air, internal recirculation occurs. Around the primary air nozzles, an arrangement of secondary nozzles feeds secondary air to the burnout zone. This staged combustion reduces both flame temperature and oxygen concentration during some phases of combustion, in turn, produces both lower thermal NO<sub>x</sub> and fuel NO<sub>x</sub> generation. Low NO<sub>x</sub> Burners should be fitted to all new plant and retrofitting to existing plant should normally be expected. Low NO<sub>x</sub>-Burners are effective in reducing NO<sub>x</sub> emissions by 30-50% [1] [5] and can be combined with other primary measures such as overfire air, reburning or flue gas recirculation.

### Secondary measures (post combustion NO<sub>x</sub> control technology)

Selective Catalytic Reduction (SCR) is the most mature and widely applied process for the reduction of nitrogen oxides in exhaust gases from combustion installations in Europe and other countries such as Japan and the U.S. The SCR process can be used for a wide range of fuels such as natural gas. The SCR process usually uses ammonia as a reducing agent, which is directly injected into the flue gas over a catalyst in the presence of sufficient oxygen. NO<sub>x</sub>-conversion takes place on the catalyst surface at a temperature between 170 and 510°C (with a range between 300 and 400°C being more typical; the minimum flue gas temperature is dependent on the sulphur content of the fuel. At a too low flue gas temperature ammoniumbisulphate is formed which will clog the SCR element) [3] NO<sub>x</sub> emission reductions over 80-90% are achieved and depend on the system design, catalyst activity and the concentration of reacting gases [2].

Selective Non-Catalytic Reduction (SNCR) reduces  $NO_x$  and operates without a catalyst at a temperature between 850 and 1100°C. This temperature window is strongly dependent on the

reactant used, which can be: ammonia, urea or ammonia solution. The SNCR process has found application for various types of fossil fuels. The average achievable  $NO_x$  abatement efficiency is in the range of 30-50% [3]. SNCR is less costly than SCR because of the absence of catalyst and can be applied also at small installations. But SNCR is not well suited for plants, which are operated at variable load (risk of excessive ammonia slip and smell).

### BAT for reducing nitrogen oxide emissions

### Combustion of lignite and coal

For NO<sub>x</sub> removal of off-gases from coal and lignite combustion plants, the use of a combination of primary and/or secondary measures is considered to be BAT. However according to the boiler technology and coal type (e.g. high primary NO<sub>x</sub> for low volatile coals) a distinction of BAT has to be made.

The combination of primary measures in combination with secondary measures such a SCR is considered to be BAT for base load pulverized coal combustion plants.

The use of a combination of different primary measures for pulverized lignite-fired plants is considered to be BAT. Because of lower  $NO_x$  emissions in lignite-fired plants, the SCR technique is not considered to be BAT for the combustion of lignite.

The use of staged combustion for the fluidized bed combustion of coal and lignite is considered to be BAT.

### Combustion of biomass and peat

For  $NO_x$  removal of off-gases from biomass and peat combustion plants, the use of a combination of primary and/or secondary measures is considered to be BAT. However according to the boiler technology a distinction of BAT has to be made.

### **Combustion of liquid fuels**

For NO<sub>x</sub> removal of off-gases from liquid-fuel fired combustion plants, the use of a combination of primary and/or secondary measures such as a SCR is considered to be BAT for over 50 MW<sub>th</sub> and in particular for large baseload plants above 100MW<sub>th</sub>.

The use of a combination of different primary measures is considered to be BAT for combustion plants with a capacity of less than 100  $\rm MW_{th}.$ 

#### **Combustion in Gas Turbines**

For new gas turbines, dry low  $NO_x$  premix burners (DLN) are BAT. For existing gas turbines, water and steam injection as primary measure or conversion to the DLN technique is BAT. DLN burners are only BAT for new turbines where the technique is available on the market for the use in gas turbines burning liquid fuels.

 Table 2: emission sources and selected BAT NOx control measures with associated emission levels in combustion installation (PM is for primary measures)

Emission source	Combination of control measures	NO <sub>x</sub> emission level associated with BAT <sup>1</sup> (mg/Nm <sup>3</sup> ) [3]		
Boilers 50 - 100 MW <sub>th</sub>				
		200 - 300		
Grate firing, Fuel: coal and lignite	PM and or SNCR	(split view industry: existing plants: 200-400)		
Boiler; Fuel: coal	Combination of PM, SNCR or SCR	90 - 300 (split view industry: new plants: 90-450, existing plants: 90-500)		
Boiler; Fuel: lignite	Combination of PM	200 - 450 (split view industry: existing plants: 200-500)		
Circulating FBC; Pressurised FBC Bubbling FBC, Fuel: coal, lignite	Combination of PM	200 - 300		
Grate firing, Fuel: biomass and peat	Spreader-stocker	170 - 250 (new) 200 - 300 (existing)		
Boiler; Fuel: biomass and peat	Combination of PM or SCR	150 - 250 (new)		
Doner, i del biornado ana pear		150 - 300 (existing)		
Circulating FBC; Bubbling FBC,	Combination of PM	150- 250 (new)		
Fuel: biomass and peat		150 - 300 (existing)		
	Combination of PM	150- 300 (new)		
Boiler, Fuel: oil	SCR	150 - 450 (existing)		
	SNCR in case of HFO firing	(split view industry: new plants: 150-400)		
		50 - 100 (new and existing)		
Industrial boiler; fuel: gas	Low NO <sub>x</sub> -Burners or SCR or SNCR	(split view industry: new and existing: 50-120)		
	Boilers 100 - 300 MW <sub>th</sub>			
Boiler; Fuel: coal	Combination of PM in combination with SCR or combined techniques	90-200 (new) 90 - 200 (existing) (split view industry: new plants: 100-200, existing plants: 90-300)		
Boiler; Fuel: lignite	Combination of PM	100 - 200 (new) 100 - 200 (existing) (split view industry: existing plants: 100-450)		
Circulating FBC; Pressurized FBC Bubbling FBC, Fuel: coal, lignite	Combination of PM, if necessary, together with SNCR	100 - 200 (new) 100 - 200 (existing) (split view industry: existing plants: 100-300)		
Boiler; Fuel: biomass and peat	Combination of PM, if necessary SNCR and/or SCR	150 - 200 (new) 150 - 250 (existing)		
Circulating FBC; Bubbling FBC, Fuel: biomass and peat	Combination of PM	150 - 200 (new) 150 - 250 (existing)		
Boiler, Fuel: oil	Combination of PM in combination with SNCR, SCR or combined technique	50 - 150 (new) 50 - 200 (existing) (split view industry: new plants:		

		50-200; existing plants: 50-450)	
Industrial boiler; fuel: gas	Low NOx burners or SCR or	50 - <del>120</del> -100 (3% O2)	
industrial bolier, ruei. gas	SNCR	(split view industry: 50-120)	
	Boilers >300 MW <sub>th</sub>		
	Combination of PM in	90 - 150 (new)	
Boiler; Fuel: coal	combination with SCR or combined techniques	90 - 200 (existing)	
		50 - 200 (new)	
Boiler; Fuel: lignite	Combination of PM	50 - 200 (existing)	
		(split view industry: new plants: 100-200; existing plants: 100-450)	
Circulating EBC: Brocourized		50 - 150 (new)	
Circulating FBC; Pressurized FBC Bubbling FBC, Fuel: coal,	Combination of PM	50 - 200 (existing)	
lignite		(split view industry: existing plants: 100-200)	
Poilor: Fuel: biomage and post	Combination of PM, if	50 - 150 (new)	
Boiler; Fuel: biomass and peat	necessary SCR or and SNCR	50 - 200 (existing)	
Circulating FBC; Bubbling FBC,	Combination of PM, if	50 - 150 (new)	
Fuel: biomass and peat	necessary SCR or and SNCR	50 - 200 (existing)	
	Combination of PM in	50- 100 (new)	
Boiler, Fuel: oil	combination with SCR or	50 - 150 (existing)	
	combined techniques	(split view industry: new plants: 50-200; existing plants: 50-400)	
New CCGT without supplementary firing	Dry low-NOx premix burners or SCR	20-50	
	Dry low-NOx premix burners	20-90	
Existing CCGT without	or water and steam injection	(split view industry existing plants:	
supplementary firing	or SCR if required space	80-120)	
New CCGT with supplementary	Dry low-NOx premix burners		
firing	and low-NOx burners for the	20-50	
	boiler part or SCR or SNCR		
	Dry low-NOx premix burners or water and steam injection	20-90	
Existing CCGT with	and low-NOx burners for the	(split view industry existing plants:	
supplementary firing	boiler part or SCR if required	80-140)	
	space in the HRSG or SNCR	,	
Industrial boiler; fuel: gas	Low NOx burners or SCR or	50 - 100 (3% O <sub>2</sub> )	
	SNCR	(industry split view: 50-120)	
	Existing Gas-Turbines		
Fuel: natural gas	Water and steam injection or	50-90	
	SCR	(industry split view: 80-120)	
Fuel: diesel oil or process gas	Water and steam injection or SCR		
	New Gas-Turbines		
Fuel: natural gas	Dry low-NO <sub>x</sub> premix burner or SCR	20-50	
Fuel: diesel oil or process gas	Wet controls SCR		

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

If not stated otherwise, values are daily averages assuming an oxygen content by volume in the waste gas of 3 % in the case of liquid and gaseous fuels, 6 % in the case of solid fuels and 15 % in the case of gas turbines.

#### 7.3.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

Dust is emitted from the combustion process, especially from the use of heavy fuel oil, coal and solid biomass. Dust emissions of solid fuel combustion are higher than dust emissions from fuel oil combustion. Because-In such large combustion, BC content of dust is very low due to very high combustion efficiency generally achieved. BC is formed during incomplete combustion and is,-it-is mainly associated to particles with a diameter less than 1 µm. In such large combustion installations, BC concentrations in dust can increase during start-up and shut-down periods in which incomplete combustion conditions can occur. A smooth, continuous and optimised combustion reduces dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC) emissions as described in chapter 6.4. Only reduction techniques able to remove fine particles have a significant efficiency on BC emissions. In such large combustion installations, BC concentrations of dust increase during start-up periods. BC content of dust is then very low due to very high combustion efficiency. The proven technologies for dust removal in power plants are fabric filters and electrostatic precipitators (ESPs) [6].

**Electrostatic precipitators (ESPs)** are the dust emissions control technology, which is most widely used in coal-fired power generating facilities [5]. They remove particles from a flowing gas using electrical forces. The particles are given an electrical charge by forcing them to pass through a corona, a region in which gaseous ions flow. The electrical field that forces the charged particles to the walls comes from electrodes maintained at high voltage in the centre of the flow lane [7].

These control devices remove dust, including particulate matter less than or equal to 10 and 2.5 micrometers and hazardous air pollutants that are in particulate form, such as most metal oxides [7]. Electrostatic precipitators are used in both solid and liquid fired combustion plants and are available for small and large-scale combustion plants [1]. ESPs provide high dust and fine particulate removal efficiency (and consequently BC which is a component of fine particulates if present). The efficiency of ESPs is described in chapter 6.5.

**Fabric filters (Baghouses),** are widely used worldwide for removing particles. A fabric filter unit consists of one or more isolated compartments containing rows of fabric bags in the form of round, flat, or shaped tubes, or pleated cartridges. Particle-laden gas passes up along the surface of the bags then radially through the fabric. Particles are retained on the upstream face of the bags, and the cleaned gas stream is vented to the atmosphere [8]. This control devices remove dust, including particulate matter less than or equal to 10 and 2.5 micrometers and hazardous air pollutants that are in particulate form, such as most metal oxides [9]. The choice between ESP and fabric filtration generally depends on coal type, plant size, and boiler type and configuration [5]. Fabric filters provide high dust and fine particulate removal efficiency (and consequently BC which a component of fine particulates if present). The efficiency of fabric filters is described in chapter 6.5.

Wet scrubbers, are air pollution control devices that remove dust and acid gases from waste gas streams of stationary point sources provided that the PM level is already within the right range to guarantee safe operation of the scrubber (if not another PM control technology is required upstream the FGD). The low capital cost of wet scrubbers compared to that for ESPs and baghouses makes them potentially attractive for industrial scale use, though this may be offset by a relatively high pressure drop and operating costs [3]. The pollutants are removed primarily through the absorption of

the pollutant onto droplets of liquid. The liquid containing the pollutant is then collected for disposal. There are numerous types of wet scrubbers, which remove both acid gas and dust.

#### BAT for the removal of dust

### Combustion of coal and lignite

For dust removal of off-gases from coal- and lignite-fired new and existing combustion plants, BAT is the use of an ESP or a FF, where a FF normally achieves emission below 5 mg/m<sup>3</sup>. Cyclones and mechanical collectors alone are not BAT, but they can be used as a pre-cleaning stage. BAT associated emission levels for dust are lower for combustion plants over 100 MWth, especially over 300MWth because the wet FGD techniques which are already a part of the BAT conclusion for desulphurisation also reduce dust [10].

### Combustion of biomass and peat

For dust removal from off-gases from biomass- and peat-fired new and existing combustion plants, BAT is the use of FF or an ESP. When using low sulphur fuels such as biomass, the potential for reduction performance of ESPs is reduced with low flue-gas sulphur dioxide concentrations. In this context, the FF, which leads to dust emissions around 5 mg/Nm<sup>3</sup>, is the preferred technical option to reduce dust emissions. Cyclones and mechanical collectors alone are not BAT, but they can be used as a pre-cleaning stage [10].

### **Combustion of liquid fuels**

For dust removal from off-gases from new and existing liquid fuel-fired combustion plants, BAT is the use of an ESP or a FF. Cyclones and mechanical collectors alone are not BAT, but they can be used as a pre-cleaning stage. BAT associated emission levels for dust are lower for combustion plants over 300 MWth because the FGD technique that is part of the BAT conclusion for desulphurisation also reduces dust [10].

Table 3: emission sources and selected BAT dust control measures with associated emission levels in combustion installation (PM is for primary measures)

Emission source	Combination of control measures	Dust emission level associated with BAT <sup>1</sup> (mg/Nm <sup>3</sup> ) [3]	
	boilers 50 - 100 MW <sub>th</sub>		
Boiler; Fuel: coal and lignite ESP or FF		< 5 - 20 (new) (split view industry: new plants: 10-50) 5-30 (existing) (split view industry: existing plants: 20- 100)	
Circulating FBC, Fuel: coal, lignite	ESP or FF		
Boiler; Fuel: biomass and peat Circulating FBC; Bubbling FBC Fuel: biomass and peat	ESP or FF	< 5 - 20 (new) 5 - 30 (existing)	
Boiler, Fuel: oil	ESP or FF	< 5 - 20 (new) 5 - 30 (existing) (split view industry: new and existing plants: 10-50 ESP)	
Boilers 100 – 300 MW <sub>th</sub>			

Boiler; Fuel: coal and lignite	ESP or FF in combination with FGD	< 5–20 (new) 5-25 (existing) (split view industry: new plants: 10-30; existing plants: 10-100 ESP/FF; 10-50 in combination with wet FGD)
Circulating FBC, Fuel: coal, lignite	ESP or FF	< 5–20 (new) 5-25 (existing) (split view: new plants: 10-30; existing plants: 10-100 ESP/FF; 10-50 in combination with wet FGD)
Boiler; Fuel: biomass and peat Circulating FBC; Bubbling FBC; Fuel: biomass and peat	ESP or FF	< 5 - 20 (new) 5 - 20 (existing)
Boiler, Fuel: oil	ESP or FF in combination with FGD	< 5 - 20 (new) 5 - 25 (existing) (split view industry: new plants: 5-30, existing plants: 5- 50)
	Boilers >300 MW <sub>th</sub>	· · · · ·
Boiler; Fuel: coal and lignite	ESP or FF in combination with FGD	< 5 - 10 (new) 10 –20 (existing) (split view industry: new plants: 10-30, existing plants: 10-100; 10-50 comb. wet FGD)
Circulating FBC; Fuel: coal, lignite	ESP or FF	< 5 –20 (new) 5-20 (existing) (split view industry: new plants: 10-30, existing plants: 10-100; 10-50 comb. wet FGD)
Boiler; Fuel: biomass and peat Circulating FBC; Bubbling FBC Fuel: biomass and peat	ESP or FF	< 5 - 20 (new) 5 - 20 (existing)
Boiler; Fuel: oil	ESP or FF in combination with FGD	< 5 - 10 (new) 5 - 20 (existing) (split view industry: new plants: 5-30, existing plants: 5-50) dard conditions and represents a typical

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

If not stated otherwise, values are daily averages assuming an oxygen content by volume in the waste gas of 3 % in the case of liquid and gaseous fuels, 6 % in the case of solid fuels.

# 7.3.4 Cost data for emission reduction techniques

## 7.3.4.1 Cost data for NOx emission reductions

Table 4: indicative costs of  $NO_x$  emissions abatement techniques for boiler plants (1999 Euros, Environment Agency)

Control options	Typically achievable emission reduction	Process capacity (MWel)	Indicative capital cost € /kWel	Indicative operating cost€ /kWh
SCR <sup>1</sup>	80-90%	Various	30-70 <sup>2</sup>	11-14 €/kWel/a <sup>2</sup>
SNCR	30-50%	Various	14	0.0011
Reburning	50-75%	Various	42	0.0011
Flue gas recirculation	15-45%	Various	14	0.00014
Low NO <sub>x</sub> Burner	30-50%	Various	14	0

<sup>1</sup> It should be noted that the design of SCR is highly site-specific and this makes definition of capital cost difficult

<sup>2</sup> J. Theloke, B. Calaminus, F. Dünnebeil, R. Friedrich, H. Helms, A. Kuhn, U. Lambrecht, D. Nicklaß, T. Pregger, S. Reis, S. Wenzel (2007): Maßnahmen zur Einhaltung der Emissionshöchstmengen der NEC Richtlinie, Umweltbundesamt, Texte 36/07, 498 pp. (cost data on p. 162)

### 7.3.4.2 Cost data for SOx emission reductions

Table 5 shows the indicative costs ranges for the sulphur abatement technologies described above. However, when applying these technologies to individual cases, it should be noted that investment costs of emission reduction measures will depend among other things on the particular technologies used, the required control systems, the plant size, the extent of the required reduction and the timescale of planned maintenance cycles. Operation and maintenance costs for SO<sub>2</sub> scrubbers for boiler plants increase with increasing sulphur content since more reagent is required to treat the same volume of gas [11].

Table 5: indicative costs of  $SO_2$  emissions abatement techniques for boiler plants (2001 Euros, EPA)

Control option	Process capacity MW <sub>th</sub>	Capital cost € /kW	O&M Cost €/kW	Annual Cost €/kW	Cost per ton of Pollutant Removed €/ton
Wet scrubber	>400	104 - 262	2 - 8	21 -52	210 -523
Wet scrubber	<400	262 - 1572	8- 21	52 - 210	523 - 5230
Dry Scrubber	>200	41- 157	4- 11	21 - 52	157 - 314
Dry Scrubber	<200	157 - 1572	11 - 314	52 - 523	523 - 4190

### 7.3.4.3 Cost data for dust emission reductions

Table 6: indicative costs of dust emissions abatement techniques for boiler plants (1999 Euros, Environment Agency)

Control options	Typically achievable emission reduction	Process capacity	Indicative capital cost €/kW	Indicative Operating cost €/kWh
ESP	Reduction to below 25 mg/m <sup>3</sup>	various	35	0.00042
Fabric filters	Reduction to below 25 mg/m <sup>3</sup>	various	14	0.0015

# 7.3.5 References used in chapter 7.3

[1] Technical background documents for the actualisation and assessment of UN/ECE protocols related to the abatement of the Transboundary Transport of nitrogen oxides from stationary sources, DFIU, 1999

[2] Environment Agency, 2002: V2. 03 27.07.05, IPPC Sector Guidance Note Combustion Activities

[3] European Commission. 2006: Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques for Large Combustion Plants

[4] Multipollutant emission control technology options for coal fired power plants, US EPA 2005.

[5] http://www.iea-coal.org.uk/site/ieacoal/home

[6] IFC 2007. International Finance Corporation (World Bank Group): Environmental, Health, and Safety Guidelines for Thermal Power Plants

[7] US Environmental Protection Agency (US EPA). EPA-452/F-03-028, Air Pollution Control Technology Fact Sheet- Dry Electrostatic Precipitator (ESP)-Wire-Plate Type

[8] US Environmental Protection Agency (US EPA). EPA-452/B-02-001, Section 6, Chapter 2, Wet Scrubbers for Particulate Matter

[9] US Environmental Protection Agency (US EPA). EPA-452/F-03-026.025.024, Air Pollution Control Technology Fact Sheet-Fabric Filters

[10] UNECE 2006. Draft background document: Assessment of technological developments: Best Available Techniques (BAT) and limit values. Submitted to the Task Force on Heavy Metals of UNECE CLTRAP

[11] US Environmental Protection Agency (US EPA). EPA-452/F-03-034, Air Pollution Control Technology Fact Sheet-Flue Gas Desulphurisation-Wet, Spray Dry, and Dry Scrubber

# 7.4 Mineral Oil and Gas Refineries for SO<sub>2</sub>, NOx dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and balck black carbon) emissions

## 7.4.1 Coverage

The section covers emissions from combustion processes in refineries burning non-commercial fuels or a mixture of commercial and non-commercial fuels, Fluidised Catalytic Cracking (FCC) units, Sulphur Recovery Units (SRU) and flares.

Refinery fuels are highly variable in nature and comprise both liquid and gaseous streams often used in conjunction. A significant part of the fuel used for process heaters is provided by refinery gas. Various processes contribute a large variety of compounds to the refinery gas, resulting in varying emissions. Other fuels in use in mineral oil refineries are natural gas, petroleum coke, heavy fuel oil, or other gaseous or liquid residues originating from atmospheric and vacuum distillation, fluid catalytic cracking (FCC) and thermal catalytic cracking (TCC). Refinery processes such as FCC may involve combustion of coke laid down on the catalyst and CO as well as supplementary fuel for steam raising. Use of petroleum coke as a gasification feedstock occurs but is not very common

Many refinery units discharge through a common stack. The emissions from refineries associated with the key processes in this chapter are  $NO_x$ ,  $SO_x$  and dust (including  $PM_{10}$ ,  $PM_{2.5}$  and black carbon (BC)). BC is an inseparable part of fine particles. Its emissions from combustion units are low as these emissions are linked to may occur during incomplete combustion <u>not frequent in this activity.</u> Incomplete combustion may occurencountered during start-up, shut-down and soot-blowing periods and if the installation is not operated in optimised combustion condition. Flares can be a source of BC emissions.

A work is still progress to revise the BREF document on refineries dated 2003 [3], at the Institute for Prospective Technological Studies (IPTS) in Seville. The 2003 document is the main reference for most of the BAT AELs presented in this chapter.

### 7.4.2 Emission sources

In the following, the focus is on emissions from processes used in the production of refined products from crude oil. These include process heaters and boilers, power generation and recovery, catalytic cracking, sulphur recovery and flare systems.

#### Process heaters and boilers

In most refining processes it is necessary to apply heat to raise the temperature of the feedstock to a required level. Fired process heaters and boilers are the main heat producers. Process heaters are installed at the atmospheric distillation, before the vacuum distillation, before the FCC units and before the hydrotreatment units. Refineries can have many process heaters, with different feedstock [1].

**Gas turbine installations** are used for the transformation of thermal energy into mechanical energy. They use a steady flow of a gas (mostly air), compressed and fired with (sometimes non-commercial) gaseous or liquid fuel. The energy in the turbine exhaust gas can be recovered in a heat recovery section downstream of the gas turbine. This heat recovery section comprises of a steam boiler or a process heater which can be equipped with additional fuel supply. Steam turbines are used to transform the steam pressure to power. Combined cycle processes combine the gas and steam turbines processes to produce power at higher efficiency than reached with open-cycle turbines.

(Fluid) Catalytic cracking (FCC) is the most widely used conversion process for upgrading heavier hydrocarbons into more valuable lower boiling hydrocarbons. It uses heat and a catalyst to break larger hydrocarbon molecules into smaller, lighter molecules. A catalytic cracking unit is usually part of a processing complex that includes a gas plant, amine treating of the light (incl. C3/C4) gases and treatment of various product streams [3].

**Sulphur Recovery Units (SRU)** typically comprise a Claus unit and a tail gas unit. They recover elemental sulphur from the  $H_2S$  recovered in the acid gas removal section. The tail gas treatment section is designed to increase the overall sulphur recovery. They work by partial combustion of the hydrogen sulphide-rich gas stream and then reacting the resulting sulphur dioxide and unburned hydrogen sulphide in the presence of a catalyst to produce elemental sulphur [3].

**Flare-Gas-System** consists at least of a flare knock-out drum and a flare stack as well as additional supporting equipment and is connected through a flare gas pipeline grid to many refinery processes. The overall goal of a flare gas system is to assure or support a pressure release of a process equipment (e.g. columns, vessels) if necessary and to keep the refinery processes in a safe condition even in an emergency case. During shut-down or start-up periods of units, e.g. before and after maintenance activities, the flare gas system has to collect off-gases for safe discharge. Flare systems are sources of SO<sub>2</sub>, NOx and dust (including BC) emissions.

# 7.4.3 BAT, Associated Emission Levels (AEL)

### 7.4.3.1 SO<sub>2</sub>

The release of sulphur dioxides is directly linked to the sulphur content of the refinery fuel gas and fuel oils used for combustion units. Heavy fuel oil residues normally contain significant proportions of sulphur and nitrogen depending mainly on their source and the crude oil [2].

Various flue gas desulphurisation techniques exist with  $SO_2$  removal efficiencies ranging from 50 to 95 to 98 %.  $SO_2$  is removed in general from the flue gas by means of wet scrubbers (lime/limestone, Wellman-Lord, seawater, wet gas sulphuric acid process WSA), spray dry scrubbers, application of sorbent injection and regenerative processes. By using wet lime/limestone reduction rates from 90 to 98% are achievable. With additive injection and spray dry scrubbers reduction rates above 92% are achievable. However, these efficiency figures are dependent on input concentrations, sizes of units and their specific application.

Improvement of the energy efficiency by enhancing heat integration and recovery throughout the refinery, applying energy conservation techniques and optimising the energy production/consumption is considered BAT [3].

The use of low sulphur content for the overall refinery liquid fuel pool achieved for example, by hydrodesulphurisation, is considered to be BAT and FGD for large boilers/furnaces where it is cost-effective. Fuel switching is also an option.

For **catalytic cracking**,  $SO_2$  emission reduction by using Sulphur Reducing Additives (SRA), FGD of the regenerator gas with 95 – 99 % efficiency (emission target depends on uncontrolled level) is considered BAT if economically viable [3].

Wet scrubbing (for example Wellman Lord scrubbing) is one option for FGD, a suitably well designed process will normally provide an effective removal efficiency of both  $SO_2/SO_3$  and particulates. With the inclusion of an extra treatment tower, to oxidise the NO to  $NO_2$ , NOx can also be removed partially [3].

Before elemental sulphur can be recovered in the SRU, the fuel gases (primarily methane and ethane) need to be separated from the hydrogen sulphide. This is typically accomplished by dissolving the hydrogen sulphide in a chemical solvent (absorption). Solvents most commonly used are amines [3].

For **sulphur recovery units** (SRU), it is BAT to apply a staged SRU, including tail gas treatment with the recovery efficiency given below (based on acid gas feed to the SRU), the range depends on cost effectiveness considerations [3].

Table 1: emission sources and selected BAT SOx control measures with associated emission	
levels in mineral oil refineries	

Emission source	Combination of control measures	SO <sub>x</sub> emission level associated with BAT <sup>1</sup> (mg/Nm <sup>3</sup> )[3]				
	Fuel type: refinery fuel gas					
Heaters, Boilers, Gas turbines	Use of sulphur removal techniques for fuel gas And use of monitoring	5 –20 <sup>3,</sup> when using fuel gas by cleaning refinery fuel gas				
	Fuel type: liquid fuel					
Heaters, Boilers	Combination of: Low S fuels Use of FGD techniques (where feasible and cost-effective)	50 – 850 for the total refinery liquid fuel pool				
	Catalytic cracking					
Catalytic cracking	Suitable combination of: Hydrotreatment of the feedstock if it is economically and technically viable Sulphur Reducing Additives (SRA) FGD of the regenerator gas if economically viable Sulphur Recovery Units (SRU)	10-350				
Sulphur recovery rate <sup>2</sup>	New plants Existing plants	99.5-99.9% 98.5-99.5%				

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

 $^2$  The sulphur recovery rate is the percentage of the imported  $H_2S$  converted to elemental sulphur as a yearly average

 $^3$  As values are expressed on a dry basis, this value has to be adjusted for hydrocarbon-hydrogen mixtures. The upper value range thus increases in proportion to the fuel hydrogen content having a value of 35 at a fuel H<sub>2</sub> concentration of 50% v.

Oxygen reference: dry basis, 3% for combustion (also for gas turbines (if expressed at 15%, the range for gas turbine is 7 - 17))

## 7.4.3.2 NOx

Refinery NO<sub>x</sub> emissions primarily originate from combustion units and catalytic cracking. Besides the relevance of the fuel type, NO<sub>x</sub> emissions depend on fuel nitrogen content (for liquid fuels) or hydrogen content and C3+ content (for gaseous fuels), burners and heaters design, and operating conditions [4].

In general, the reduction of the fuel consumption and the replacement of existing burners with low-NOx burners during major scheduled shutdowns is considered to be BAT as far as is possible with respect to the existing process engineering design.

For heaters and boilers burning gaseous fuel an application of a suitable combination of the following primary and secondary measures allowing to achieve emissions levels from 20 to 150 mg/Nm<sup>3</sup> is considered to be BAT [3]:

- high thermal efficiency furnace/boiler designs with good control systems
- jowlow-NO<sub>x</sub> burners technique
- flue gas circulation in boilers
- SCR or SNCR

For heaters and boilers burning combinations of gas and liquid fuel (liquid fuel as majority fuel) an application of a suitable combination of the following primary and secondary measures allowing to achieve emissions levels from 55 to 300 mg/Nm<sup>3</sup> is considered to be BAT [3]:

- fuel with low nitrogen content
- low-NO<sub>x</sub> burners technique
- flue gas circulation in boilers
- reburning technique
- SCR or SNCR to liquid fuels heavier than gasoil type (if technically and economically feasible)

For gas turbines an application of a suitable combination of the following primary and secondary measures allowing to achieve emissions levels from 20-75 mg/Nm<sup>3</sup> is considered to be BAT [3]:

- diluent injection
- dry low NOx combustors
- SCR (if technically and economically feasible)

# Table 2: emission sources and selected BAT NOx control measures with associated emission levels in mineral oil refineries

Emission source	One or combination of control measures	NO <sub>x</sub> emission level associated with BAT <sup>1</sup> (mg/Nm <sup>3</sup> ) [3]		
	Fuel type: refinery fuel gas			
Heaters, Boilers	<ul> <li>high thermal efficiency designs with good control systems</li> <li>low-NO<sub>x</sub> burners technique</li> <li>flue gas circulation in boilers</li> <li>SCR or SNCR (if technically and economically feasible)</li> </ul>	20 – 150 <sup>2</sup>		
Gas turbines burning either gas or light liquid fuels	<ul> <li>diluent injection</li> <li>dry low NOx combustors</li> <li>SCR (where technically and economically applicable)</li> </ul>	20 – 75 (lower levels for natural gas and higher levels for small gas turbines and RFG)		
Fuel type: heavy liquid fuel firing (majority fuel)				
Heaters, Boilers	<ul> <li>liquid fuel with low nitrogen content</li> <li>low-NO<sub>x</sub> burners technique</li> <li>flue gas circulation in boilers</li> <li>SCR or SNCR to liquid fuels heavier than gasoil type (where technically and economically applicable)</li> </ul>	55 – 300 <sup>2</sup>		
	Catalytic cracking			
	CO-furnace/boiler for partial oxidation conditions	100-300		
Catalytic cracking	for full combustion plants	300-600		
	Combination of (if economically viable): modification of the design and operation of regenerator, SCR, SNCR	40-150		
<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded. <sup>2</sup> in the EU-BREFof 2003, several split views exist about BAT AELs.				

Oxygen reference: dry basis 3% for combustion, 15 % for gas turbines

### 7.4.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

The main emission sources of dust in refining are process heaters and boilers firing liquid heavy fuel oil, catalytic cracker regenerators, coke plants, incinerators, decoking and soot blowing of heaters and the flare <u>[3]</u>.

The emission levels of dust depend on various parameters such as fuel type, burner design, and oxygen concentration at the outlet of the radiant section and can vary widely.

The dust emissions from furnace and boilers burning heavy fuel oil consist of a mix of-ash, soot and BC. Mineral matter is a natural component of crude oil and becomes ash during combustion of heavier fuel oils. Soot and BC result from imperfections in the combustion process. BC content of dust is low in continuous processes with optimised combustion conditions but can be higher during start-up and shut-down periods in which imcomplete combustion condition can occur.

The size of the particulate matter from heaters and boilers burning heavy fuel oil is in the order of 1  $\mu$ m. Particulate matter removal techniques mainly used are ESPs. An application of a suitable combination of the following techniques is considered to be BAT for the reduction of dust 3:

- Reduction of the fuel consumption
- Maximizing the use of gas and low ash content liquid fuels
- Improved atomisation on the liquid fuels
- The use of ESP or filters in the flue gas of heaters and boilers when burning heavy liquid fuels [3] if technically and economically feasible.

Emission source	One or combination of control measures	Dust emission level associated with BAT <sup>1</sup> (mg/Nm <sup>3</sup> )
	Fuel type: heavy liquid fuel (majority fuel)	
	By a combination of:	
	- Reduction of the fuel consumption	5 – 20 [3]
Heaters, boilers	- Maximizing the use of gas and low ash content liquid fuels	(split view industry:
2011010	- Steam atomisation on the liquid fuels	5-50)
	- Use of ESP	
	By a suitable combination of:	
FCC	process integrated measures,	10 10 <sup>2</sup>
regenerators	ESP,	10-40 <sup>2</sup> [5]
	third stage cyclones, scrubbers	
<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typica		

# Table 3: Emission sources and selected BAT dust control measures with associated emission levels in mineral oil refineries

load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

<sup>2</sup> If technical difficulties in upgrading the existing ESPs, the upper range can be difficult to reach. In those cases 50 is seen as a more achievable value [3].

Oxygen reference: dry basis, 3% for combustion, 15 % for gas turbines.

### BAT for flare systems:

Flare systems can be equipped with adequate monitoring and control systems necessary to operate smokelessly and should be observed at all times under non emergency conditions to avoid emissions. Techniques to be applied to flares that may reduce emissions (including BC) [3] are:

- the pilot burners give more reliable ignition to the vent gases because they are not affected by the wind
- steam injection in flaring stacks can reduce particulate matter emissions
- coke formation in flare tips should be prevented
- surplus refinery gas should be flared, not vented. Knock-out pots to remove liquids should be
  provided, and with appropriate seals and liquid disposal system to prevent entrainment of
  liquids into the combustion zone. Water streams from seal drums should be routed to the sour
  water system
- flare-gas recovery systems have been developed due to environmental and economic considerations. The flare gas is captured and compressed for other uses. Usually recovered flare gas is treated and routed to the refinery fuel gas system. Depending upon flare gas composition, recovered gas may have other uses. Reductions of flaring to ratios of 0.08 0.12 % of production in one natural gas plant in Norway have been reported. Flare gas recovery is not cost effective if the flow of gas to flaring is reduced by other measures.

# 7.4.4 Emerging techniques

Emerging techniques in the field of  $SO_2$  emission reduction are  $SO_2$  capture from flue gas and subsequent conversion into liquid sulphur as well as biological H<sub>2</sub>S removal [3].

Integrated gasification combined cycle (IGCC) is a technique for producing steam, hydrogen and electric energy from a variety of low-grade fuel types. The gasified solid fuel is burned in the combustion chamber of the gas turbine. Emissions from IGCC are low. The technology also exists for heavy oil residue. However, this process is not yet fully commercialized for refeneries, a number of demonstration units, mainly around 250 MWe size are being operated in Europe and the USA.

## 7.4.5 References used in chapter 7.4

[1] O. Rentz, D. Oertel: Process Furnaces, SNAP Code 01 03 06, In: Atmospheric Emission Inventory Guidebook, CD-Rom, 1996

[2] Environment Agency: Guidance for the gasification, liquefaction and refining sector, 2003

[3] European commission: Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries, Integrated Pollution Prevention and Control (IPPC), February 2003

[4] O. Rentz, S. Nunge, M. Laforsch, T. Holtmann: Technical Background Document for the Actualisation and Assessment of UN/ECE Protocols related to the Abatement of the Transboundary Transport of Nitrogen Oxides from Stationary Sources, Task Force on the Assessment of Abatement Options/Techniques for Nitrogen Oxides from Stationary Sources, Karlsruhe, September 1999

[5] J. Schacht, J. Courtheyn: ESP units realise major dust emission reduction at Total Refinery Antwerp. Total Refinery Antwerp, presented at Dustconf 2007

[6] Concawe Report 4/09 "Refining BREF review – Air Emissions" Prepared by the CONCAWE Air Quality Management Group's Special Task Force on Integrated Pollution Prevention and Control (AQ/STF-70), 2009

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# 7.5 Mineral oil and gas refineries for VOC emissions

# 7.5.1 Coverage

This chapter covers activities originating VOC emissions in the oil refineries: fugitive emissions, flare system, storage tanks, and oil separators. Fugitive VOC emission sources (such as leakages from flanges, pumps or any pieces of equipment) and losses from the storage facilities of liquid products may contribute more than 50 % to the total VOC emissions. VOC emissions also occur from processes linked to combustion and from flares but these are lower emitters of VOCs in refineries. The refinery petrol dispatch station is covered by chapter 7.20.

# 7.5.2 Emission sources

Sources of VOC emissions considered are as follows:

# Fugitive emissions:

Fugitive VOC emissions are released from leaking pressurised equipment components on process units, such as valves, flanges and connectors, opened lines and sampling systems containing volatile liquids or gases. Volatile products are defined in CEN 15446 [9] and reference [10] as all products of which at least 20% by weight has a vapour pressure higher than 0.3 kPa at 20C.

The quantity of VOC emissions from sealing elements, depends on:

- size, type and material of the seal,
- state of maintenance, age of the equipment,
- pressure, temperature, and physical condition of the product. Emissions are larger at those refineries that are processing light products (fuel producing refineries).
- valves represent 50-60 % of fugitive emissions [1]. A major portion of fugitive emissions comes from only a small portion of sources (less than 1 % of valves in gas / vapour service may account for more than 70% of the fugitive emissions of a refinery).

# The flare systems:

Flares are used for safety and environmental control of discharges of undesired or excess combustibles and for surges of gases in emergency situation or upsets [1]. The VOC emissions from flaring itself are a small proportion of the total refinery VOC emissions. Fugitive emissions, however, can result from leaking equipment components in the flare gas collection system.

# The oil water separators:

Waste water treatment systems employed in refineries include neutralisers, oil/water separators, settling chambers, clarifiers, dissolved air flotation systems and activated sludge ponds. If contaminated by oil, the waste water from a refinery is passed to a multi-stage water purification via an oil separator or via flocculation.

Emissions from sewage systems and oil separators primarily result from evaporation of NMVOC from liquid surfaces open to the atmosphere. Direct sources include processes that use water for washing (e. g. desalter), sour water stripping and also steam used in jet eductors to produce vacuum. Indirect sources include leaks from heat exchangers, condensers and pumps.

Sources of contamination with hydrocarbons are [4]:

- desalters: 40 %
- storage tanks: 20 %
- slop systems: 15 %
- other processes: 25 %

# Crude oil and volatile product storages:

A significant proportion of the VOC emissions from refineries may arise from storage tanks for crude oil and volatile products in case of no use of BAT. Those products may be stored in different types of storage tanks according to the physical and chemical properties, such as fixed roof tanks, external floating roof tanks or internal floating roof tanks. Fixed roof tanks can only be used for petroleum products with very low vapour pressure.

# 7.5.3 BAT, associated emission levels (AEL)

BAT for reducing VOC emissions are as follows [1] and [2]:

# Fugitive emissions:

- quantifying VOC emission source in order to identify the main emitters in each specific case,
- executing leak detection and repair programme (LDAR) campaigns or equivalent. A good LDAR includes the determination of the type of measurement frequency, type of components to be checked, type of compound lines, what leaks should be repaired and how fast action should be taken,
- using a maintenance drain out system,
- selecting and using low leakage valves such as graphite packed valves or equivalent for lines containing product with high vapour pressure,
- using low leak pumps (e.g. seal less designs, double seals, with gas seals or good mechanical seals) on lines containing product with high vapour pressure,
- blinding, plugging or capping open ended vents and drain vents,
- routing relief valves with high potential VOC emissions to flare,
- routing compressor vents with high potential for VOC emissions back to process and when not possible to refinery flare for destruction,
- using totally closed loop in all routine samplers that potentially may generate VOC emissions,
- minimizing flaring.

A LDAR programme is established according to the following principles [3]:

- 1 the definition of what constitutes a leak and fixation of corresponding thresholds,
- 2 the fixation of the frequency of inspections,
- 3 the listing and identification of components included,
- 4 the procedures concerning repair of leaking components depending on the leak category.

Equipment tightening can be made with equipment in operation (except with remote control valves (e.g. tightening bolts to eliminate leaks from valves stems or flanges, installing tightening caps on open ends...)., etc).

Maintenance with equipment dismantling or exchange can only be implemented during plant shutdowns with circuit insulation and degassing. This implies that implementing this type of maintenance with the sole objective of reducing fugitive emissions would lead to unacceptable costs.

Maintenance on the equipment can consist in removing some parts or replacing the equipment with a new one of the same technology (named basic maintenance in this document). A complete change of equipment such as valves with valves of the newest not leaking technology can also be operated (not considered in this document).

# Water treatment plant [1]:

 covering separators, basins and inlet bays and by routing off gases in the waste water treatment plant. Implementation of some of these techniques may compromise efficient operation of the waste water treatment plant or cause safety concerns if they are not properly designed and managed. For these reasons, this technique may have some technical problems when retrofitted.

# Storage and handling [1] and [2]:

- ensure that the liquids and gases stored are in appropriate tanks or vessels based upon the true vapour pressure of the stored materials,
- use high efficiency seals in floating roof tanks (example provided in reference [1] indicates an incremental reduction potential for changing from a vapour mounted primary seal to a liquid mounted seal was 84%),
- bund all stored chemicals, with separate bunding for incompatibles,
- apply emission reduction measures during tank cleaning,
- apply concept of good house keeping and environmental management,
- minimise the number of tanks and volume by suitable combination of application of in line blending, integration of processing units, these techniques being much easier to apply on new facilities, e.g. by vapour balance lines that transfer the displaced vapour from the container being filled to the one being emptied. Incompatibility of tank vapours and applicability to external floating roofs tank are some examples of restrictions of application. Applicability needs to reflect economics, the type and size of vessel to be used (e.g. tank, truck, railcar, ship), type of hydrocarbon fraction and frequency of use of the tank. Because this technique is related to the next one, both should be evaluated together when implementing on a specific site.
- apply vapour recovery (not applicable to non-volatile products) on tanks, vehicles, ships etc. in stationary use and during loading/unloading. Achieved emission levels are very dependent on the application, but recoveries of 95 >99 % are considered BAT. If VRUs are not considered appropriate for certain streams, vapour destruction units are considered BAT. Properties of streams, such as type of substance, compatibility of substances or quantity need to be considered in the applicability of this BAT. Applicability needs to reflect economics, the type and size of vessel to be used (e.g. tank, truck, railcar, ship), type of hydrocarbon fraction and frequency of use of the tank. Because this technique is related to the above one, both should be evaluated together when implementing on a specific site.
- reduce the risk of soil contamination by the implementation of an inspection maintenance programme which can include good house keeping measures, double bottom tanks, impervious liners...
- install self sealing hose connections or implement line draining procedures,
- some other best practices.

External floating roofs and internal floating roofs can have the following emission reduction efficiency: The BAT associated emission reduction level associated to an external floating roof for a large tank is at least 97 % (compared to a fixed roof tank without measures), which can be achieved when over at least 95 % of the circumference the gap between the roof and the wall is less than 3.2 mm and the seals are liquid mounted, mechanical shoe seals. By installing liquid mounted primary seals and rim mounted secondary seals, a reduction in air emissions of up to 99.5 % (compared to a fixed roof tank without measures) can be achieved [2].

The achievable emission reduction for a large tank using an internal floating roof is at least 97 % (compared to a fixed roof tank without measures), which can be achieved when over at least 95 % of the circumference of the gap between the roof and wall is less than 3.2 mm and the seals are liquid mounted, mechanical shoe seals. By applying liquid mounted primary seals and rim mounted secondary seals, some further improvement in emission reductions can be achieved. However, the smaller the tank and the smaller the numbers of turnovers are, the less effective the floating roof is.

However, measurements of diffuse sources (e.g. tanks) can only be made over short periods and extrapolation to provide annual estimates of emissions introduces significant errors due to the temporal variations in emissions from these types of sources.

Table 1: associated Emission	Levels with BAT to reduce	VOC emissions from storage

Emission sources	Combination of BAT	BAT Associated Emissions Levels for VOCs
Storage tanks of volatile products	Internal floating roof External floating roof Other tank designs and appropriate colours	97 to 99.5 % compared to a fixed roof tank without measure*

\* If the efficiency cannot be reached because of the specific characteristics of a storage tank (such as small throughput, small diameter), best available primary and secondary seals have to used.

# Table 2: associated Emission Levels with BAT to reduce VOC emissions in refinery loading and unloading operations

Emission source	BAT and reduction efficiency	BAT associated emission levels* kg VOC/m <sup>3</sup> /kPa [1], [6]
Road tanker filling, bottom or top loading and vapour balancing during previous off loading and VRU		0.0228 x 0.05 to 0.0228 x 0.01
Rail tanker, top loading and VRU	VRU with 95 to 99 % efficiency [1]	0.0108 x 0.05 to 0.0108 x 0.01
Marine tanker, typical cargo tank condition		0.004 x 0.05 to 0.004 x 0.01
Barge – typical cargo tank conditions		0.007x 0.05 to 0.007 x 0.01

\*Not available in reference [1] but calculated with reference [6].

kPa: True vapour of the volatile product.

# 7.5.4 Cost data for emission reduction techniques

The EGTEI synopsis sheet [7] on VOC emissions in refineries provides costs of VOC emission reduction techniques.

Cost of a LDAR programme depends on the thresholds defining what constitutes a leak. Reference [1] provides operating costs ranging from 0.04 to 0.08 M $\in$ /year for a 10000 ppm programme and 0.8 M $\in$ /year for a 100 to 500 ppm.

# 7.5.5 References used for chapter 7.5

[1] European Commission - Reference document on best available techniques for mineral oil and gas refineries - BREF – February 2003 – European commission – Available at: <u>http://eipccb.jrc.es</u>

[2] European Commission - reference document on BAT on emissions from storage – February 2003July 2006 – Available at: <u>http://eipccb.jrc.es</u>

[3] EGTEI - background document on the organic chemical industry - 2003

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[6] CONCAWE - Air pollutant emission estimation methods for E-PRTR reporting by refineries - Report n°1/2009 (Amending report 2007)

[7] EGTEI synopsis sheets on NMVOC from refineries – October 2005

[8] EPA - Emission factor documentation for AP42 section 7.1 - Organic liquid storage tanks - Final report - September 2006

[9] EN15446:2008 Fugitive and diffuse emissions of common concern to industry sectors - Measurement of fugitive emission of vapours generating from equipment and piping leaks

[10] EPA - Protocol for equipment leak - Emission estimates EPA 453-95-017 - 1995

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# 7.6 Coke oven furnaces

## 7.6.1 Coverage

This section deals with emissions originating from coke oven furnaces in iron and steel production. The further use of coke or coke oven gases is not regarded here, for information see section "Iron and Steel Production".

# 7.6.2 Emission sources

Within the production of primary iron and steel, the blast furnace (<u>cf. Refer to</u> section "Iron and Steel Production") is the main operational unit. Coke is basically used as a reducing agent in a blast furnace due to its physical and chemical characteristics. It is produced from coal in a coke oven via dry distillation.

**Coke oven plant:** Coke is produced via heating of coal mixtures in absence of oxygen. The coke oven is a chamber made up of heat resistant bricks. A heating wall consists of heating flues with nozzles for fuel supply and with air intakes. In general, cleaned coke oven gas is used as a fuel as well as other gases such as blast furnace gas. The coke is afterwards used mainly as a reducing agent in blast furnaces.

Due to high costs of coke, replacement by pulverized coal, fuel oil, plastics etc. may replace it as reducing agents in the blast furnace route [2]. This reduction in coke consumption also helps to reduce total emissions from coke production. Several 'direct' and 'smelting reduction' processes have been developed for primary iron production without the use of coke (for example Corex).

### 7.6.3 BAT, Associated Emission Levels (AEL)

### 7.6.3.1 SO<sub>2</sub>

In general emissions of SO<sub>2</sub> can be minimised by reducing the sulphur content of the coal.

During the coking process, this sulphur of the coal is fully converted into  $H_2S$  and captured with the coke oven gas, which is used usually after cleaning of the coke oven gas <u>i.a.for instance</u> as fuel for coke oven underfiring. Hence, the emissions of SO<sub>2</sub> can be minimized by the use of coking coal with lower sulphur content, as well as by adequate desulphurisation of the coke oven gas. For underfiring coke oven gas and blast furnace gas can be used.

The use of desulphurised coke oven gas is considered to be BAT. And the desulphurization of coke oven gas by absorption systems or the oxidative desulphurization is considered to be BAT.

The prevention of leakage between oven chamber and heating chamber by means of regular coke oven operation is considered to be BAT [2]. Table 1 shows selected BAT  $H_2S$  control measures with associated  $H_2S$  levels of the coke oven gas (to be later used as a fuel i.a. for coke oven underfiring).

#### Table 1: selected BAT H<sub>2</sub>S control measures with associated H<sub>2</sub>S levels of coke oven gas [2]

Combination of control measures	H₂S level mg/Nm <sup>3</sup>
Desulphurisation by absorption systems	500 -1000
Oxidative desulphurization	< 500
	Desulphurisation by absorption systems

The BAT associated emission levels may be expected to be achieved over a substantial period of time at standard conditions and represents a typical load situation.

According to the German IPPC implementation report from 2006 the SOx-emissions from coke oven plants in Germany - all applying COG desulphurisation - were in the magnitude of 110-250 mg/m3 when using solely COG (90% percentile values based on half-hourly average values from continuous measurements). When using mixed gas (a mix mainly consisting of COG and blast furnace gas), the reported emissions were in the range of 80-160 mg/m<sup>3</sup>.

### 7.6.3.2 NO<sub>x</sub>

### Coke oven gas

Nitrogen emissions arising from the coke oven firing result mainly from the thermal and the <del>chemical</del> <u>fuel</u> NOx mechanisms (refer to chapter 3.4, for the description of the different mechanisms). Chemical Fuel NOx is due to the residual content of nitrogen compounds in the COG after cleaning e.g. ammonia. Nevertheless, the type of fuel used is also of importance [1].

The most effective way to reduce the formation of  $NO_x$  is achieved by reducing the flame temperature in the heating chamber [1]. Therefore, the  $NO_x$  emissions from the coke oven firing are preferably minimised by process-integrated measures, but end-of-pipe techniques may also be applied. However, due to the high cost, flue gas denitrification (e.g. SCR) is currently not applied except in a limited number of new plants under circumstances where environmental quality standards are not likely to be met [2].

The use of combustion modification techniques such as, low-NO<sub>x</sub> techniques, staged combustion are considered to be BAT in new batteries. Achievable  $NO_x$  emissions are 500-770 mg/Nm<sup>3</sup>.

# Table 2: Emission sources and selected BAT NOx control measures with associated emission levels in coke ovens [2]

Emission source	Combination of control measures	NO <sub>x</sub> emission level associated with BAT <sup>1</sup> mg/Nm <sup>3</sup>
Combustion of coke oven gas	Combustion modification (at new plants)	500-770 (5% O <sub>2</sub> ) <sup>2</sup>

<sup>1</sup> The BAT associated emission levels may be expected to be achieved over a substantial period of time at standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

<sup>2</sup> German IPPC implementation report from 2006 the NOx-emissions from coke oven: 322-414 mg as annual average values from different plants (using both solely COG or mixed gas).

### 7.6.3.3 Dust (including PM10, PM2.5 and black carbon)

Information on emissions from blast furnaces that use coke oven gas can be found in the section "Iron and steel production".

Emissions of dust in coke ovens arise mainly from diffuse dust emission sources at the coking plant, starting from coal handling and processing, diffuse emissions from charging holes, coke oven doors and coke pushing, until coke quenching.

Coke ovens are a significant source of BC in developing countries according to references [4] and [5]. In western countries emissions are controlled and limited. Monitoring data are very scarce. Dust emissions may contain a share of black carbon. Measures reducing dust emissions may consequently reduce black carbon emissions when those measures are efficient on fine particles. Emissions of dust (including  $PM_{10}$ ,  $PM_{2.5}$  and black carbon) should be prevented by minimising charging emissions (<del>cf.</del> table 3), by sealing the openings efficiently and good maintenance, by minimising leakage between coke oven chamber and heating chamber and especially by using de-dusting of coke pushing. Dust in the waste gas from coke oven underfiring can be removed by means of fabric filters or ESP [2], [3].

Table 3: Emission sources and selected BAT dust control measures with associated emission levels in coke ovens [2]

	mg/Nm <sup>3</sup> or (kg/tonne)
"Smokeless" charging or sequential charging With double ascension pipes or jumper pipes are the preferred; efficient evacuation and subsequent combustion and fabric filtration	(< 5 g/t coke)
Extraction with an (integrated) hood on coke transfer machine and land-based Extraction gas treatment with fabric filter and usage of one point quenching car	(< 5 g/t coke (stack emissions))
Wet quenching	(< 50 g/t coke)
Coke dry quenching (CDQ)	< 5 mg/m <sup>3</sup> (< 6-12 g/t coke)
	Vith double ascension pipes or jumper pipes are the preferred; ifficient evacuation and subsequent combustion and fabric iltration Extraction with an (integrated) hood on coke transfer machine and land-based Extraction gas treatment with fabric filter and usage of one point juenching car Vet quenching

standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

# 7.6.4 Emerging techniques

Due to high costs and environmental impacts from coke use, 'direct' and 'smelting reduction' processes may replace the blast furnace route and hence make coke production unnecessary [2].

So-called super coke ovens aim at, amongst others, reduced  $NO_{\boldsymbol{X}}$  and dust emissions.

# 7.6.5 References used in chapter 7.6

- Technical background documents for the actualisation and assessment of UN/ECE protocols related to the abatement of the Transboundary Transport of nitrogen oxides from stationary sources, DFIU, 1999.
- [2] European commission: Best Available Techniques Reference Document on the production of Iron and Steel, December 2001.
- [3] European commission: Best Available Techniques Reference Document on the production of Iron and Steel, Draft February 2008.
- [4] UNEP/WMO Integrated Assessment of Black Carbon and Tropospheric Ozone 2011.
- [5] UNECE Ad Hoc Expert Group on Black Carbon Black carbon Report by the Co-Chairs of the Ad Hoc Expert Group on Black Carbon. Executive Body for the Convention on Long-range Transboundary Air Pollution. Twenty-eighth session Geneva, 13–17 December 2010.

# 7.7 Iron and steel production

## 7.7.1 Coverage

The sector covers iron and steel making in integrated steelworks (sinter plants, pelletization plants, coke oven plants, blast furnaces and basic oxygen furnaces including continuous and ingot casting) and electric arc furnace steelmaking [1]. Other downstream activities like ferrous metal processing in foundries, rolling or galvanizing are dealt with within the sector "ferrous metals processing". Emissions originating from coke oven furnaces in iron and steel production are dealt with in the section coke ovens.

## 7.7.2 Emission sources

The iron and steel industry is a highly material and energy intensive industry, in which more than half of the mass input becomes output in the form of off-gases and solid wastes/by-products. Air emissions from sinter plants dominate the overall emissions for most of the pollutants. Besides sinter plants, most relevant emissions occur in pelletization plants, coke oven plants (described in the separate section for this sector), blast furnaces, basic oxygen steelmaking and casting, and electric steelmaking and casting [1], [2].

### Sinter plants

Sinter is the product of an agglomeration process of iron-containing materials and is the source of a major part of environmental issues in integrated steel works. This product is obtained by heating a layer of crushed and mixed raw material (iron ore, coke, limestone ...) and by exhausting flue gases through this layer so that the surface melts and agglomerate is formed. Sinter plants are playing a very important role for the internal material management of integrated steel works because, under conditions, most of iron-bearing waste materials can be recycled into the sinter feed in order to utilise their iron content and consequently save raw material. The off-gas emissions from sinter strands contain pollutants such as dust, heavy metals, SO<sub>2</sub>, HCI, HF, PAH and organochlorine components [1], [3].

Sinter plants are not recognized as a significant source of BC according to references [10], [11] and [13]. Monitoring data are very scarce.

### **Pelletization plants**

Pelletization is an alternative process to agglomerate iron-containing materials, with pellets being produced mainly at the site of the mine or its shipping port. Again, emissions to air dominate the environmental issues [1], [9].

Pelletization plants are not recognized as a significant source of BC according to references [10], [11] and [13]. Monitoring data are very scarce.

**Coke oven plants** are not subject of this part, but are dealt with in chapter 7.6.

### Blast furnaces

The blast furnace remains by far the most important process to produce pig iron from iron containing materials. These are reduced using carbon and hot gas to pig iron, which later acts as a raw material for steelmaking. Due to the high input of reducing agents (coke, pulverized coal) it consumes most of the overall energy input in an integrated steelworks [1]. It produces a high volume of process gas, which needs to be cleaned before being used for internal combustion or for internal/external generation of energy.

Although the blast furnace route is the main process for iron production, several other production routes for pig iron are currently being developed. Two main types of alternative iron making are direct reduction (production of solid primary iron from iron ores and a reducing agent, e.g. natural gas) and smelting reduction (combining direct reduction in one reactor with smelting in a separate reactor, without the use of coke). COREX is a commercially successful version of a 'smelting reduction'

process [4]. These techniques use coke, coal or natural gas as the reduction agent. In some of the new techniques lump ore and pellets by pulverized iron ore as the main feedstock. The solid product is called Direct Reduced Iron (DRI) and is mainly applied as feedstock in EAFs [4], [9].

Blast furnaces are not recognized as a significant source of BC according to references [10], [11] and [13]. Monitoring data are very scarce.

### Basic oxygen steelmaking and casting

The objective of oxygen steelmaking is to reduce the carbon content and to remove the undesirable impurities still contained in the hot metal from the blast furnace. It includes the pre-treatment of hot metal, the oxidation process in the basic oxygen furnace, secondary metallurgical treatment and casting (continuous and/or ingot). In addition to hot metal, up to 25% scrap can be used as input material. Collected basic oxygen furnace (BOF) gas is cleaned and stored for subsequent use as a fuel, if economical feasible or with regard to appropriate energy management [1], [4].

Basic Oxygen oxygen furnaces are not recognized as a significant source of BC according to references [10], [11] and [13]. Monitoring data are very scarce.

### Electric steelmaking and casting

The direct smelting of iron-containing materials, mainly scrap, is usually performed in electric arc furnaces. This needs considerable amounts of electric energy and causes substantial emissions to air. The energy consumption (and the corresponding amount of  $CO_2$  emissions) from steel production in electric arc furnaces is about one third of the energy consumption of the blast furnace / basic oxygen furnace route. The use of this 'lower  $CO_2$  production route' is however limited by the availability of scrap and certain qualities of steel can only be achieved via the primary production route [1].

Electric <u>arc</u> furnaces are not recognized as a significant source of BC according to references [10], [11] and [13]. Monitoring data are very scarce.

# 7.7.3 BAT, Associated Emission Levels (AEL)

### 7.7.3.1 SO<sub>2</sub>

For **sinter plant** emissions,  $SO_2$  can be minimised by lowering the sulphur input (use of coke breeze and iron ore with low sulphur content), emission concentrations of <500 mg  $SO_2/Nm^3$  can be achieved in this way.  $SO_2$  emissions from sinter plants may also be reduced by dry or semi-dry adsorption systems in combination with high-efficiency dust filters (as part of a multi-pollutant control technique).

With a wet waste gas desulphurization, reduction of  $SO_2$  emissions >98% and concentrations < 100 mg  $SO_2/Nm^3$  can be achieved. Due to the high cost wet waste gas desulphurisation should only be required in circumstances where environmental quality standards are not likely to be met [1] operational reliability (availability ratio of the equipment) is also questioned.

For **pelletization plants**, dust,  $SO_2$  and other pollutants can be removed from induration strand waste gas either by scrubbing or semi-dry desulphurization and subsequent de-dusting (e.g. gas suspension absorber (GSA)) or by any other device with the same removal efficiency [1].

Addition of adsorbents such as hydrated lime, calcium oxide or fly ashes with high calcium oxide content may be used to further reduce  $SO_2$  emissions, when injected into the exhaust gas outlet before filtration [9].

Emission Source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments
Sinter plants [1]	< 500 (1)	500 according to BREF
Pelletization plants [1]	< 20	SO <sub>2</sub> as SO <sub>2</sub> ; using system with removal efficiency >80%
Blast furnaces: cowpers (hot stoves)	< 200	Related to an oxygen content of 3% In the German IPPC implementation report from 2006 a range of 60-210 mg/m <sup>3</sup> is reported as 5% and 95% percentiles based on half-hourly average values from continuous measurements.

Table 1: SO<sub>2</sub> emission levels associated with BAT for iron and steel production

<sup>1</sup> The BAT associated emission levels may be expected to be achieved over a substantial period of time at standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

# 7.7.3.2 NOx

For **sinter plants**, NO<sub>x</sub> emissions should be minimized by, for example waste gas recirculation, waste gas denitrification using regenerative activated carbon process or selective catalytic reduction. Regenerative activated carbon and selective catalytic reduction are options for reducing NO<sub>x</sub> emissions, but have not yet been applied in the UN-ECE region on full scale due to their high costs (currently SCR is tested in pilot plant scale at one European steel plant) [1].

For **pelletization plants** it is considered BAT to optimise plant design for recovery of sensible heat and low-NO<sub>x</sub> emissions from all firing sections (induration strand, where applicable and drying at the grinding mills) [1]. For one pelletization plant, NO<sub>x</sub> emissions of 175 g/tonne pellet are achieved using process-integrated measures only, namely by a combination of low energy use, low nitrogen content in the fuel (coal and oil) and limiting the oxygen excess [5], [6].

The application of modern burners may reduce NOx emissions of to blast furnace cowpers.

Emission Source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments
Blast furnace (hot stoves) [1]	20-120	Related to an oxygen content of 3% In the German IPPC implementation report from 2006 a range of 20-120 mg/m <sup>3</sup> is reported as 5% and 95% percentiles based on half-hourly average values from continuous measurements.
Sinter plants <sup>1</sup> [6]	300-400 100-120 <sup>2</sup>	Normal operation conditions SCR <sup>3</sup>

<sup>1</sup> The BAT associated emission levels may be expected to be achieved over a substantial period of time at standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

<sup>2</sup> The emission level is based on data from Japan and Taiwan

<sup>3</sup> Due to the high cost, waste gas denitrification is not applied except in circumstances where environmental quality standards are not likely to be met.

### 7.7.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

Fabric filters should be used whenever possible, reducing the dust content to less than 20 mg/m<sup>3</sup> (hourly average). If conditions make this impossible (due to their tendency to blind and their sensitivity to fire), advanced ESPs and/or high-efficiency scrubbers may be used, reducing the dust content to 50 mg/m<sup>3</sup>. Many applications of fabric filters can achieve much lower values [4], [7].

**Sinter plants** may generate the most significant quantity of dust emissions in integrated steel mills, they arise primarily from material handling and from the agglomeration reaction on the strand.

Dust (together with PCDD/F) is furthermore the most important pollutant in sinter plants and waste gas de-dusting is considered BAT, for example by application of advanced electrostatic precipitation (moving electrode ESP, ESP pulse system, high voltage operation of ESP) or electrostatic precipitation plus fabric filter or pre-dedusting (e.g., ESP or cyclone) plus high pressure wet scrubbing system. The presence of fine dust, which mainly contains alkali and lead chlorides may limit the efficiency of ESPs.

BAT also includes to use enclosure and/or hooding, where appropriate, with emission controls, of the sinter strand operations that are potential sources of fugitive emissions, as well as to apply operating practices that minimize fugitive emissions that are not amenable to enclosure or hooding. For reducing dust emissions from material handling operations indoor or covered stockpiles, when possible, as well as a simple and linear layout for material handling should be used. Enclosed conveyer transfer points and enclosed silos to store bulk powder can further reduce emissions from bulk powder materials (fugitive emissions of coal dust are a major concern here) [1], [4], [9].

BC emission monitoring data are scarce. When present in dust, BC emissions can be removed, at least partially, by the use of the same BAT measures described just above for dust when those measures are efficient for the concerned size of particles.

For information for **pelletization plants** see above (chapter 7.7.3.1).

For **blast furnace** gas treatment, an efficient de-dusting is considered BAT using dry separation techniques (e.g. deflector) for removing and reusing coarse particulate matter. Subsequently fine particulate matter is removed by means of a scrubber or a wet electrostatic precipitator or any other technique achieving the same removal efficiency. For cast house de-dusting, emissions should be minimized by covering the runners and evacuation of the emission sources (tap-holes, runners, skimmers, torpedo ladle charging points) and purification by means of fabric filtration or electrostatic precipitation [1].

BC emission monitoring data are scarce. When present in dust, BC emissions can be removed, at least partially, by the use of the same BAT measures described just above for dust when those measures are efficient for the concerned size.

For **basic oxygen steelmaking and casting** including hot metal pre-treatment, secondary metallurgical treatment and continuous casting (including hot metal transfer processes, desulphurization and deslagging), BAT is considered to use particulate matter abatement by means of efficient evacuation and subsequent purification by means of fabric filtration or electrostatic precipitation. For basic oxygen steelmaking and casting, the use of a whirl hood for secondary dedusting aims at reducing dust emissions.

Basic oxygen furnace gas recovery and primary de-dusting is considered BAT applying suppressed combustion and dry electrostatic precipitation (in new and existing installations) or scrubbing (in existing installations). Secondary de-dusting is considered BAT applying efficient evacuation during charging and tapping with subsequent purification by means of fabric filtration or ESP or any other technique with the same removal efficiency. Efficient evacuation should also be applied during hot metal handling, deslagging of hot metal and secondary metallurgy with subsequent purification by means of fabric filtration or any other technique with the same removal efficiency.

No BC emissions occur according to reference [12]. When present in dust, BC emissions can be removed, at least partially, by the use of the same BAT measures described just above for dust when those measures are efficient for the concerned size.

For **electric steelmaking and casting**, BAT is considered to achieve dust collection efficiencies with a combination of direct off gas extraction (4th or 2nd hole) and hood systems or dog-house and hood systems or total building evacuation of 98% (primary and secondary emissions). Waste gas de-dusting is considered BAT using well designed fabric filters achieving 5 mg dust/Nm<sup>3</sup> for new plants and 15 mg dust/Nm<sup>3</sup> for existing ones, both determined as daily mean values [1].

No BC emissions occur according to reference [12]. BC emission monitoring data are however scarce. When present in dust, BC emissions can be removed, at least partially, by the use of the same BAT measures described just above for dust when those measures are efficient for the concerned size.

### Table 3: Dust emission levels associated with BAT for iron and steel production

[Comment: [9] recommends maximum dust emission levels of 50 mg/Nm<sup>2</sup> for all operations in integrated steel mills, 20 mg/Nm<sup>2</sup> when toxic metals are present]

	Emission Source	BAT associated emission levels <sup>1</sup>	Comments
		mg/Nm <sup>3</sup> or (kg/tonne)	
	Sinter Plants	< 50 [1]	Existing sinter plants equipped with advanced ESPs
		10-20 [1]	Application of fabric filters
		(0.04-0.12) [4]	
	Pelletization plants	10 [1]	Using a system with removal efficiency
	r elletization plants	(0.04) [4]	>95%
		< 10 [1]	Related to an oxygen content of 3%
	Blast furnaces: Hot stoves	(0.035-0.05) [4]	kg/tonne pig iron
	Blast furnaces: fugitive emissions (fully captured)	(0.005-0.015) [1]	US EPA 1998 [1][8] reports the following shares of PM <sub>1</sub> in dust: Casthouse (older type): 15%; Furnace with local evacuation: 9%; Hot metal desulphurization: 2%
		5-15 [1]	Fabric filters
	Basic oxygen steelmaking	20-30 [1]	ESP
	and casting	(0.035-0.07) [4]	US EPA 1998 [8] reports the following shares of PM <sub>1</sub> in dust: Charging (at source) 12%;Tapping (at source) 11%
		< 5 <sup>2</sup> [1][1]; (0.06) <sup>3</sup> [4]	For new plants
	Electric steelmaking and	$< 15^{2}$ [1]; (0.12) <sup>3</sup> [4]	For existing plants
	asting	····· (······ (······ / [·]	US EPA 1998 [8] [8] reports the following shares of PM <sub>1</sub> in dust for EAF: Melting and refining (carbon steel, uncontrolled): 23%

<sup>1</sup> The BAT associated emission levels may be expected to be achieved over a substantial period of time at standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

<sup>2</sup> For this value: daily mean

<sup>3</sup> Recommended performance indicator

Note:

The International Finance Corporation [9] recommends maximum dust emission levels of 50 mg/Nm<sup>3</sup> for all operations in integrated steel mills, 20 mg/Nm<sup>3</sup> when toxic metals are present.

In the Iron & Steel Industry BREF document, there is to emphasize that only the air emissions at EAF and the water data at Blast Furnace are expressed as daily averages when all other BAT AELs have been expressed under normal operation conditions (e.g. excluding start up and shut down periods) and design, and averaged on a substantial period of time (there is not yet any consensus reached about this definition)

# 7.7.3.4 VOC

Volatile organic compounds and polycyclic aromatic hydrocarbons (PAH) may be emitted from various stages in iron and steel production. These include off gases in the pelletization and sintering

processes due to carbon compounds contained in the solid fuels of sinter or pelletization feed, for example from the addition of mill scale [9].

As this sector is not considered a major emitter of VOC, no further information is given on emission levels associated with BAT.

#### 7.7.3.5 Cross Media Effects

For all mentioned emission reduction and abatement techniques, the cross-media transfer of pollutants and the full range of environmental effects and improvements should be considered. For example additional energy consumption and increased quantities of waste or wastewater residuals may result from individual efforts for pollutant prevention, reduction, or removal.

Especially de-dusting using ESP or FF leads to an additional solid waste flow, which can be recycled into the process for some cases. If the bags in FF are precoated by injecting slaked lime, significant abatement of some acidic components (HCI, HF) can also be achieved. In combination with an injection of lignite coke or activated carbon, FF also help to reduce PCDD/PCDF emissions significantly (to below 0.1 to 0.5 ng/m<sup>3</sup>). The minimisation of dust emissions correlates with the minimisation of heavy metal emissions except for heavy metals in the gas phase like mercury [1], [2].

# 7.7.4 Emerging techniques

Direct reduction and direct smelting are under development (<u>cf-refer to</u> section description of production technologies) and may reduce the need for sinter plants and blast furnaces in the future.

The use of new reagents in the hot metal desulfurization process might lead to a decrease in dust emissions and a different (more useful) composition of the generated dust. The technique is under development. Several foaming techniques at pig iron pre-treatment and steel refining are already available, absorbing the dust arising from the hot metal processing [4].

For electric arc furnaces, intermetallic bag filters combine filtering and catalytic operations and allow to reduce dust and associated pollutant emissions [2]. Additionally, a number of new furnace types have been introduced, that might be realized at industrial scale, and that show advantages with regard to heavy metals and dust emissions, e.g.:

Comelt EAF (integrated shaft scrap preheating and a complete off gas collection in each operating phase)

Contiarc furnace (waste gas and dust volumes are considerably reduced, and the gas-tight furnace enclosure captures all primary and nearly all secondary emissions)

# 7.7.5 Cost data for emission reductions

8 Table 4: examples of investments and operating costs of control options for the abatement of NOx emissions [6]

7.7.5

Characteristics of reference installation	Control options	Investments <sup>ª/</sup> [EURO]	Operating costs <sup>⊵⁄</sup> [EURO/year]	Abated mass flov [Mg NO <sub>x</sub> /year]
Source: previous guidan	ce document			_
Iron and steel producti	on: sinter plant		1	
Travelling grate sinter machine; Fuel: coke		5,000,000	- 200,000 <del>≌⁄1</del>	2,000
breeze; Production output: 12,000 Mg sinter/day;	SCR	50,000,000	5,300,000	3,200
Operating time: 8,400 h/year				

<sup>1</sup> Due to reduced coke breeze consumption

<u>(Comment: UNECE 2006 states "Total costs of implementing FFs for one representative sinter plant are 3000 to 16000 Euro p.a."</u>]

# 7.7.6 References used in chapter 7.7

- [1] European Commission. 2001: "Integrated Pollution Prevention and Control (IPPC) Best Available Techniques Reference Document on the Production of Iron and Steel." <u>http://eippcb.jrc.es/pages/FActivities.htm</u>
- [2] European Commission. 2008 Draft: "Integrated Pollution Prevention and Control (IPPC) Best Available Techniques Reference Document on the Production of Iron and Steel." http://eippcb.jrc.es/pages/FActivities.htm
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: 0 pt, Sans numérotation ni puces

- [12] Kupiainen, K. & Klimont, Z., 2004. Primary Emissions of Submicron and Carbonaceous Particles in Europe and the Potential for their Control. International Institute for Applied Systems Analysis (IASA), Interim report IR-04-79, Schlossplatz 1 A-2361 Laxenburg Austria.
- [13] EPA Report to congress on black carbon March 2012.

# 7.8 Ferrous metals processing including iron foundries

#### 7.8.1 Coverage

This section on ferrous metals processing comprises iron foundries (for continuous and ingot casting see chapter "Iron and steel production") with a capacity exceeding 20 tonnes/day, as well as installations for "hot and cold forming", including hot rolling, cold rolling, wire drawing, installations for "continuous coating", including hot dip coating and coating of wire, and installations for "batch galvanizing" [1], [2].

# 7.8.2 Emission sources

#### 7.8.2.1 Foundries

Foundries melt metals and alloys (only ferrous metals regarded in the following) and reshape them into products at or near their finished shape through the pouring and solidification of the liquid metal into a mould. Fluxes and fuels are similar as in pig iron processing. The industry consists of a wide range of installations, most of them comprising the process steps: melting and metal treatment, preparation of moulds and core, casting the molten metal in the mould, cooling for solidification and removing, finishing the raw casting. The main environmental issues of this industry are emissions to air (dust, acidifying compounds, products of incomplete combustion and volatile organic compounds) [2], [3].

#### 7.8.2.2 Hot and cold forming

In **hot rolling**, the size, shape and metallurgical properties of steel are changed by repeatedly compressing the hot metal (1050-1300 °C) between rollers. The steel input varies in form and shape – cast ingots, slabs, blooms, billets, beam blanks – depending on the product, generally classified in the basic types flat and long products. Hot rolling mills usually comprise the following process steps: conditioning of the input (scarfing, grinding); heating to the rolling temperature; descaling; rolling and finishing. The main environmental issues of hot rolling are emissions to air, especially NO<sub>X</sub> and SO<sub>2</sub>, energy consumption and dust emissions.

In **cold rolling**, the properties of hot rolled strip products (thickness, mechanical and technological characteristics) are changed by compression between rollers without previous heating. The process steps for low alloy steel (carbon steel) are pickling, rolling for reduction in thickness, annealing or heat treatment to regenerate the crystalline structure, temper rolling or skin pass rolling of annealed strip to give desired mechanical properties and finishing. The process steps for high alloy steel (stainless steel) involves additional steps, the main stages are: hot band annealing and pickling, cold rolling, final annealing and pickling (or bright annealing), skin pass rolling and finishing. The main environmental issues of cold rolling are acidic waste and waste water, degreaser fume acidic and oil mist emissions to air, dust and NO<sub>x</sub> (mixed acid pickling and furnace firing).

**Wire drawing** is a process in which wire rods/wires are reduced in size by drawing them through cone-shaped openings of a smaller cross section, called dies. A typical plant comprises the following process lines: pre-treatment (descaling, pickling), dry or wet drawing, heat treatment and finishing. The main environmental aspects of wire drawing are air emissions from pickling, acidic wastes and waste water, fugitive soap dusts, spent lubricants and combustion gases [1].

#### 7.8.2.3 Continuous hot dip coating

In the hot dip coating process, steel sheet or wire is continuously passed through molten metal. An alloying reaction between the two metals takes place, leading to a good bond between coating and substrate. Continuous coating lines for sheet comprise the steps surface cleaning (chemical or thermal treatment), heat treatment, immersion in a bath of molten metal, and finishing treatment. Continuous wire galvanizing plants involve the steps pickling, fluxing, galvanizing, finishing. Main environmental issues are acidic air emissions, waste and wastewater and energy consumption [1].

#### 7.8.2.4 Batch galvanizing

Hot dip galvanization is a corrosion protection process in which iron and steel fabrications are coated with zinc. Prevalent in this sector is job galvanizing, in which a great variety of products are treated for different customers; batch galvanizing usually comprises the steps degreasing, pickling, fluxing, galvanizing, finishing. The main environmental issues are emissions to air (HCI, dust) spent process solutions and oily wastes and zinc containing residues [1].

# 7.8.3 BAT, Associated Emission Levels (AEL)

#### 7.8.3.1 SO<sub>2</sub>

For re-heating and heat treatment furnaces in **hot rolling** installations, a careful choice of fuel and implementation of furnace automation/control to optimise the firing conditions is considered BAT. Process waste gases are commonly used at reheating furnaces in place of fossil fuels. Fuels with low S content are commonly used [1].

Emission Source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments	
Foundries: ferrous metal	20-100	Hot blast cupola	
melting [2]	100-400	Cold blast cupola	
	70-130	Rotary arc furnace	
Moulding and casting using lost moulds (regeneration units) [2]	120		
100		For natural gas	
Hot rolling: re-heating and heat treatment furnaces [1]	400	For all other gases and gas mixtures	
near treatment furnaces [1]	1700 <sup>2</sup>	for fuel oil <1%S	
Cold rolling: H <sub>2</sub> SO <sub>4</sub> -pickling	8-20	Recovery of the free acid by crystallisation; air scrubbing devices for recovery plant.	
Cold rolling: HCI-pickling [1]	50-100	Regeneration of the acid by spray roasting or fluidised bed (or equivalent system)	
<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas			

Table 1: SO<sub>2</sub> emission levels associated with BAT for ferrous metals production

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.
<sup>2</sup> EU-BREF split view if fuel oil <1%S is BAT or additional SO<sub>2</sub> reduction measures are necessary

# 7.8.3.2 NO<sub>x</sub>

For re-heating and heat treatment furnaces in **hot rolling** installations, the use of second generation low-NO<sub>x</sub> burners is considered BAT. [comment: BREF2001 split view on whether SCR and SNCR are BAT for re-heating and heat treatment furnaces in hot rolling installations]

For mixed acid pickling in **cold rolling** installations, it is considered BAT to use either free acid reclamation (by side-stream or ion exchange or dialysis) or acid regeneration by spray roasting or acid regeneration by evaporation process. In general for mixed acid pickling in cold rolling installations, enclosed equipment/hoods and scrubbing should be used, and additionally for high alloy steels either scrubbing with  $H_2O_2$ , urea, etc. or  $NO_x$  suppression by adding  $H_2O_2$  or urea to the pickling bath or by use of SCR. An alternative is to use nitric acid-free pickling plus enclosed equipment or equipment fitted with hoods and scrubbing. For annealing furnaces in cold rolling installations, it is BAT to use low  $NO_x$  burners for continuous furnaces, combustion air preheating by regenerative or recuperative burners or pre-heating of stock by waste gas.

For **continuous hot dip coating**, it is considered BAT to use low-NO<sub>X</sub> burners and regenerative or recuperative burner for heat treatment furnaces and galvannealing. For heat treatment furnaces, it is

additionally BAT to use pre-heating of the strip and steam production to recover heat from waste gas where there is a need for steam [1].

Table 2. NO <sup>*</sup>	emission levels associated	with <b>BAT</b> for ferrous	metals production
		with DAT for ferrous	

Emission Source	BAT associated	Comments
	emission levels <sup>1</sup>	
	mg/Nm <sup>3</sup> or (kg/tonne)	
	10-200	Hot blast cupola
Foundries: ferrous metal	20-70	Cold blast cupola
Foundries: ferrous metal melting [2]	160-400	Cokeless cupola
	10-50	Electric arc furnace
	50-250	Rotary arc furnace
Moulding and casting using lost moulds (regeneration units) [2]	150	
	390	Fuel: blast furnace gas; low NO <sub>x</sub> burner
Hot rolling: re-heating and	1100	Fuel: coke oven gas, heavy fuel oil; low $NO_X$ burner
heat treatment furnaces [1]	250-400	Fuel: natural gas, gas oil; low NO <sub>X</sub> burner $3\% O_2$ for gas, $6\% O_2$ for liquid fuel
Hot rolling: re-heating and heat treatment furnaces using SCR <sup>2</sup> and SNCR <sup>2</sup> [1]	320 <sup>3</sup> 205 <sup>3</sup>	$SCR^2$ SNCR <sup>2</sup> , ammonia slip 5 mg/Nm <sup>3</sup> 3% O <sub>2</sub> for gas, 6% O <sub>2</sub> for liquid fuel
Cold rolling: HCl pickling [1]	300-370	
Cold rolling: mixed acid pickling [1]	200-650 200 100	Acid regeneration by spray roasting Acid regeneration by evaporation process
Cold rolling: annealing furnaces [1]	250-400	Without air pre-heating, 3% $O_2$ , reduction rates of 60% for $NO_X$
Hot dip coating: heat treatment furnaces and galvannealing [1]	250-400	Without air pre-heating, $3\% O_2$

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

<sup>2</sup> EU-BREF split view if SCR and SNCR are BAT (only one of each installation exists in Europe)

<sup>3</sup> These are emission levels reported for the one existing SCR plant (walking beam furnace) and the one existing SNCR plant (walking beam furnace).

#### 7.8.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

For **foundries**, a key issue in emission reduction is not only to treat the exhaust and off-gas flow, but also to capture it. BAT is to minimize fugitive emissions arising from various non-contained sources in the process chain like from furnaces during opening or tapping by optimizing capture and cleaning, clean furnace off-gas by subsequent collection, cooling and dust removal. For cupola furnace melting of cast iron, BAT for dust reduction is to improve thermal efficiency and use a fabric filters or wet scrubbers.

For the operation of induction furnaces, BAT is, amongst others, use a hood, lip extraction or cover extraction on each induction furnace to capture the furnace off-gas and to use dry flue-gas cleaning [2].

For finishing techniques like abrasive cutting, shot blasting and fettling, BAT is to collect and treat the finishing off gas using a wet or dry system. For heat treatment, BAT is to use clean fuels (i.e. natural gas or low-level sulphur content fuel), automated furnace operation and burner/heater control and also to capture and evacuate the exhaust gas from the heat treatment furnaces.

For **hot rolling**, it is considered BAT to use enclosures for machine scarfing and dust abatement with fabric filters or electrostatic precipitators, where fabric filters cannot be operated because of wet fume. For machine grinding operations in hot rolling installations, BAT is to use enclosures for machine grinding and dedicated booths, equipped with collection hoods for manual grinding and dust abatement by fabric filters. In the finishing train, exhaust systems with treatment of extracted air by fabric filters and recycling of collected dust is considered BAT. For levelling and welding, suction hoods and subsequent abatement by fabric filters are considered BAT.

For **cold rolling**, it is BAT to use extraction hoods with dust abatement by fabric filters in levelling and welding operations.

For coating of wire, it is considered BAT to use good housekeeping measures<sup>1</sup> for hot dipping [1].

Iron and steel foundries are not recognised as a significant source of BC according to references [7], [8]. Monitoring data are very scarce. No emission factor is proposed by reference [9]. When present in dust, BC emissions can be removed, at least partially, by the use of the same BAT measures described just above for dust when those measures are efficient for the concerned size.

Emission Source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments
Iron Foundries [2]	5-20	daily average, standard conditions
Iron foundries: induction furnaces [2]	(0.2)	
Hot rolling: machine scarfing [1]	5 / 20 <sup>2</sup> 10 / 20-50 <sup>2</sup>	Fabric filters ESP, where FF cannot be operated because of wet fume
Hot rolling: grinding [1]	5 / 20 <sup>2</sup>	
Hot rolling: finishing train and levelling and welding[1]	5/ 20 <sup>2</sup>	
Cold rolling: decoiling [1]	5 / 20 <sup>2</sup>	
Cold rolling: HCl pickling [1]	20-50	
Cold rolling: levelling and welding [1]	5 / 20 <sup>2</sup>	
Coating of wire: hot dipping [1]	10	
Galvanizing baths [4]	15	

#### Table 3: dust emission levels associated with BAT for ferrous metals production

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded. <sup>2</sup> EU-BREF 2001 split view

### 7.8.3.4 VOC

In foundries, various additives are used to bind the sand in the making of moulds and cores; These include organic and inorganic compounds (solvents, BTEX, phenol, formaldehyde, etc.): the generation of decomposition products further continues during the casting cooling and de-moulding operations. As the process involves various emission sources (hot castings, sand, hot metal), a key issue is not only to treat the off-gas, but also to capture it [5].

Hydrocarbons and misted oil emissions may arise from the cold rolling mill operations, advanced emission collection and demisting systems like precoated fabric filters can be used to reduce them [6].

<sup>&</sup>lt;sup>1</sup> Cf. EIPPCB BREF 2001, Chapter B.4

#### Table 4: VOC emission levels associated with BAT for ferrous metal processing

Emission Source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments
Foundries: Ferrous metal melting	10-20	Cold blast cupola
<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.		

#### 7.8.3.5 Cross Media Effects

For all mentioned emission reduction and abatement techniques, the cross-media transfer of pollutants and the full range of environmental effects and improvements should be considered. For example additional energy consumption and increased quantities of waste or wastewater residuals may result from individual efforts for pollutant prevention, reduction, or removal.

# 7.8.4 Emerging techniques

For hot and cold rolling, the flameless burner or diffuse flame maximises recirculation of the flue gas and has punctually achieved  $NO_x$  emission levels of 100 mg/m<sup>3</sup>, however no industrial application exists until now. Reductions of NOx emissions are also aimed at by the ultra low-NOx burner (complete mixing of fuel and combustion air in the furnace, thus no anchoring of the flame in the furnace) and water injection (reduction of temperature and thus thermal NOx formation) [1].

# 7.8.5 Cost data for emission reduction techniques

Technique	Typical range of NO <sub>x</sub> reduction	Capital cost (GBP	Operating cost (GBP/GJ)	Total cost of technique (GBP '000/year for 50 MW furnace)		•
	Å	·000)	(021700)	2000 hours/year	4000 hours/year	8000 hours/year
Low-NO <sub>X</sub> burners	Up to 97%	328	0.0	53.7	53.7	53.7
Limiting air preheat		NA	0.0257 for 50 % NO <sub>x</sub> reduction	92.5	185	370
Flue gas recirculation	Up to 93% (44.74 15 % FGR)	75.6 (631)*	0.098 (0.072)*	47.6 (129)*	82.9 (154)*	153 (206)*
SCR	up to 95% (Typically 70 - 90)	1100 - 2530	0.0722	205 - 438	231 - 464	283 - 516
SNCR (with NH <sub>3</sub> )	up to 85% (Typically 50 - 60)	350 - 650	0.0361	69.9 - 119	82.9 - 132	109 - 158

Table 5: cost information for different NO<sub>x</sub> reduction techniques for a 50 MW furnace [1]

Cost given in 1996 British Pounds NA Not available and, for th

## 7.8.6 References used in chapter 7.8

- European Commission. 2001: "Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Ferrous Metals Processing Industry." <u>http://eippcb.jrc.es/pages/FActivities.htm</u>
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# 7.9 Non ferrous metal processing industry<sup>1</sup>

# 7.9.1 Aluminium

#### 7.9.1.1 Coverage

Aluminium industry is the largest non ferrous metal industry. This chapter covers primary and secondary aluminium production.

#### 7.9.1.2 Emission sources

Aluminium production is divided into 2 types of production, the primary production and the secondary production.

In **primary production**, alumina is the raw material used to produce aluminium. Alumina is produced from the bauxite, extracted from mines. Caustic soda is used to extract alumina from bauxite, using a standard process at high temperature and pressure. Aluminium is then produced by electrolytic reduction of alumina. During this process the exhaust gases are collected and treated by a dry alumina scrubber and dust treatment system such as ESP or bag filters. Further abatement systems might be considered on a case-by-case basis.

The obtained aluminium is then refined to remove impurities by injection of gas in the molten metal. The choice of the gas depends on the type of impurities. These processes are sources of dust,  $SO_2$  and  $NO_x$  emissions. [1].

In **secondary production**, aluminium comes from scraps. These scraps can be pre-treated (swarf drying or thermal de-coating) before being processed to produce aluminium.

Different furnaces, mainly rotary or reverberatory furnaces can be used to melt the raw material. Natural gas, which does not contain sulphur, is the fuel most commonly used. The obtained aluminium is then refined in a holding furnace as in the primary aluminium production. These processes are sources of dust,  $SO_2$  and  $NO_x$  emissions-[1].

## 7.9.1.3 BAT, Associated Emission Levels (AEL)

If not stated otherwise, emission levels given in this section are given as daily average based on continuous monitoring and standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas without dilution of the gases with air.

## SO<sub>2</sub>:

In primary aluminium production, SO<sub>2</sub> emissions are influenced by the sulphur content of the anodes used during the electrolytic reduction. In secondary production, and in the production of carbon anodes for the Prebake primary production, the possible source of SO<sub>2</sub> emissions is the sulphur content of the fuel used. SO<sub>2</sub> emissions do not generally cause the greatest concern during the aluminium production process, however this has to be considered on a case-by-case basis, depending on the local and environmental conditions.

In primary aluminium production, BAT to reduce  $SO_2$  emissions is to limit sulphur content fuel and anodes, subject to their market availability. For secondary aluminium production, wet or semi-dry alkaline scrubbers are considered BAT to reduce  $SO_2$  emissions from the holding and degassing of molten metal process, material pretreatment process, and melting and smelting processes.

The applicability of  $SO_2$  abatement systems has to be assessed on a case-by-case basis, taking into account the technical characteristics of the plant, the geographical location and the local conditions, with particular reference to possible cross-media effects

<sup>&</sup>lt;sup>1</sup> The information included in <u>this</u> subchapter is based on the NFM BREF.[1], which is currently under revision <del>in June 2009</del> at the Institute for Prospective Technological Studies in Sevile (IPTS).

# Table 1: associated SO<sub>2</sub> emission levels with BAT to reduce emissions in aluminium industry<sup>a/</sup> [1] [10]

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Holding and degassing of molten metal in primary and secondary aluminium production		< 50 – 200
Materials pre-treatment, melting and smelting in secondary aluminium production	wet or semi-dry alkaline scrubber (if needed)	< 50 – 100
Grinding, mixing and baking stages (if sulphur is added to the blend or the fuel contains high %S) [1]		< 50 - 200

a/ The information included in Tab. 1 is currently under discussion in the context of the NFM BREF revision, whose conclusion is anticipated in Q1 2010. It would be advisable not to include this table to avoid possible confusion once the new NFM BREF is adopted or, at least, to clarify that this information, including BAT-AELs, is under revision.

# NO<sub>x</sub>:

In aluminium production  $NO_x$  emissions come from the combustion processes used to melt the raw materials. Emissions are influenced by different parameters: the type of fuel, the type of combustion, the combustion air-ratio and the flame temperature. Oxy-fuel burner and low  $NO_x$  burners are the measures considered BAT to reduce  $NO_x$  emission in aluminium production. [1].

The following table gives an overview of achievable NO<sub>x</sub> emission levels in aluminium production.

# Table 2: associated NO<sub>x</sub> emission levels with BAT to reduce emissions in aluminium industry 11(1)

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
furnaces from primary and secondary aluminium and swarf drying	Low NO <sub>x</sub> burner Oxy-fuel burner	< 100 < 100 - 300

# Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

In primary aluminium production, dust emissions come mainly from alumina production process, electrolysis, smelting and casting processes. This source is not identified as a large emitter of BC according to references [15], [16]. BC emission data are scarce. According to [17], there is no BC emission in primary aluminium and 1.2 g BC/t aluminium produced in secondary aluminium plants.

Flue gases from production of alumina need to be collected and a fabric filter or ESP can be used to remove calcined alumina and dust. Collected gases from other processes need to be dedusted. A fabric filter can be used. A wet scrubber can also be used depending on local conditions. [6]

In secondary aluminium production, pre-treatment, secondary smelting and holding are sources of dust emissions. Ceramic or fabric filters can be used to remove dust from the collected gases of secondary smelting process. For the other processes, flue gases need to be collected and can be filtered using a fabric filter when it is needed. [1].

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The collected dust from the filters has to be reused when it is possible.

The material reception, handling and storage are sources of fugitive dust emissions. These emissions have to be minimized by a good handling and protections from the wind of raw material.

The following table gives an overview of achievable dust emission levels in aluminium production. [3]

The preferred technique for dust abatement is the use of a fabric filter or a ceramic filter.

If present in dust, BC emissions can be removed, at least partially, by the use of the same BAT measures described in table 3 for dust which are also efficient for fine particles.

# Table 3: associated dust emission levels with BAT to reduce emissions in aluminium industry [1][4], [4][4]

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Electrolysis, Pre-treatment	Fabric filter	Dust: 1 – 5
Primary & secondary smelting	Ceramic or fabric filter	

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# 7.9.2 Copper

#### 7.9.2.1 Coverage

Copper is largely used for its very high thermal and electrical conductivity, its relative resistance to corrosion and its easiness to be recycled. This category covers copper production from primary and secondary processing.

#### 7.9.2.2 Emission sources

Copper production is divided into 2 productions, the primary production and the secondary production.

#### **Primary production**

The concentrates used to produce primary copper are mainly sulphides and contain other metal than copper. Therefore several processes are used to separate the different compounds and recover them as far as possible. Due to the composition of the concentrates (sulphides), SO<sub>2</sub> emission level is high during these processes.

2 methods are used to produce primary copper: pyrometallurgical and hydrometallurgical processes.

The **pyrometallurgical process** is made of several steps: roasting, smelting, converting, refining and electro-refining.

The roasting is a major source of  $SO_2$  emissions. During the roasting, the sulphides are heated to become sulphur. The flue gases needs then to be desulphurized; they are usually directed to on-site acid plants to produce sulphuric acid or liquid  $SO_2$ .

The smelting step enables the separation between copper sulphides from other compounds contained in the ore. Roasting and smelting steps are realised in a unique furnace at high temperatures enabling the separation between the matter mainly containing copper sulphides and the slag mainly containing iron sulphides. [1].

The converting steps consist in injecting air and oxygen in the matte formerly obtained during the smelting step. The converting processes can be batch, the most used, or continuous. During these processes,  $SO_2$  emissions are also relevant.

The copper needs then to be refined; a fire refining process is first applied. During the fire refining process, air is injected to the smelting metal so as to oxide the impurities and remove the last traces of sulphur. A small reducing agent can be added but it increases  $NO_x$  emissions.

The electro-refining process takes place in an electrolytic cell using a cast copper anode and a cathode. The cell is placed in an electrolyte containing copper sulphate and sulphuric acid.

The hydrometallurgical process is mainly applied to oxide ores, oxide/sulphide ores or ores hard to concentrate. The ores are first crushed and then leached by sulphuric acid. The liquor produced during the leaching is then clarified, purified and concentrated using a solvent extraction. Copper is finally removed by electro-winning. It only differs from electro-refining in the anode form. [1].

#### Secondary production

The secondary copper is produced using pyrometallurgical processes. The steps of these processes depend on the copper content of the secondary feed material. It can contain other organic material like coatings. Therefore, secondary smelting and secondary refining are designed depending on the feed material. [1].

#### 7.9.2.3 BAT, Associated Emission Levels (AEL)

If not stated otherwise, emission levels given in this section are given as daily average based on continuous monitoring and standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas without dilution of the gases with air.

#### SO<sub>2</sub>:

In copper production,  $SO_2$  emissions cause the greatest concern. Sulphur comes mainly from the ores used to produce copper. Hence  $SO_2$  emissions are more concerning during primary production than during secondary production. Roasting, smelting and converting are the major sources of sulphur dioxide.  $SO_2$  comes from the copper sulphides used to produce copper. The roasting and smelting steps are realised in the same furnace. It needs to be sealed to enable a better collection of the gases. Oxygen enrichment is used to produce high sulphur dioxide concentration. It enables the reduction of the flue gas volumes. Sulphuric acid plants are used to convert these gases.

The converting process is also a source of  $SO_2$  emissions, but the gas collection is not totally efficient when using batch processes, due to the variation of sulphur dioxide concentration. Then  $SO_2$  removal systems need to be designed consequently. [1].

The sulphur dioxide emissions from the roasting, smelting and converting process are removed from the flue gases using a sulphuric acid plant.

The following table gives an overview of achievable SO<sub>2</sub> emissions levels in copper production.

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
SO <sub>2</sub> -rich off-stream gas (> 5 %) Primary roasting, smelting and converting	Double contact sulphuric acid plant	99.7 – 99.92 % (conversion factor)
Secondary smelting and converting, primary and secondary fire-refining, electric slag cleaning and melting.	Alkali semi-dry scrubber and fabric filter. Wet alkali or double alkali scrubbers using lime, magnesium hydroxide, sodium hydroxide. Combinations of sodium or alumina/aluminium sulphate in combination with lime to regenerate the reagent and form gypsum	< 50 – 200
Secondary fume collection	Fabric filter with dry lime injection into a cool gas	< 500
systems and drying processes	Alkaline wet scrubber for SO <sub>2</sub> collection from hot gases (from dryer gases after dust removal)	< 50 – 200

Table 4: associated SO <sub>2</sub> emission levels with BAT to reduce emissions in copper industry [1]
[11]

# NO<sub>x</sub>:

In copper production, the use of oxygen and the high temperature processes are responsible for  $NO_x$  emissions. During the primary production, nitrogen oxides are mainly absorbed in the sulphuric acid produced. Thus  $NO_x$  emissions are not a major issue. BAT to reduce these emissions are the use of oxy-fuel burners and low  $NO_x$  burners. [1].

The following table gives an overview of achievable NO<sub>x</sub> emissions levels in copper production. [1]

#### Table 5: associated NO<sub>x</sub> emission levels with BAT to reduce emissions in copper industry

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
primary and secondary copper production	Low NO <sub>x</sub> burner Oxy-fuel burner	< 100 < 100 - 300

#### Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC):

In copper production, smelting, converting and refining processes are major sources of dust emissions. In these production processes, flue gases are collected, cooled and filtered using ESP and fabric filters to control dust emissions and volatile metals contained in dust. [1], [2].

This source is not identified as a large emitter of BC according to references [15], [16]. BC emission data are scarce. According to [17], there is no BC emission in other non ferrous metal production.

The following table gives an overview of achievable dust emissions levels in copper production. The preferred technique for dust abatement is the use of a fabric filter or a ceramic filter. Electrostatic precipitators should be used for gases containing too much moist, for hot gases, or when the dust is too sticky. Scrubbers should be used as the temperature or the nature of the gases precludes the use of other techniques, or when gases or acids have to be removed simultaneously with dust.

If present in dust, BC emissions can be removed, at least partially, by the use of the same BAT measures described in table 6 for dust which are also efficient for fine particles.

 Table 6: associated dust emission levels with BAT to reduce emissions in copper industry [1]
 [3]

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Smelting, converting and refining processes	Fabric filters ESP Scrubbers	Dust: 1 – 5

## 7.9.3 Lead and Zinc

#### 7.9.3.1 Coverage

This category covers both lead and zinc production, from primary and secondary production. These metals are often associated together in ores and concentrates. As it is in the other non ferrous metal processing industry,  $SO_2$  and dust emissions are the more concerning. However  $NO_x$  emission reductions are also detailed in this category.

#### 7.9.3.2 Emission sources

As for copper or aluminium production, lead and zinc can be produced from primary or secondary processes.

There are 2 **primary lead** production processes: the sintering/smelting process and the direct smelting process. Primary zinc process is on the wane as a production method [6], [8].

The **Sintering/smelting** process involves of the agglomeration of lead and zinc concentrates, recycled sinter fines, secondary materials and other process materials.

The agglomeration product is then crushed, screened and charged into an Imperial Smelting Furnace where the smelting process takes place. Lead is directly recovered from this furnace as by product and then refined. A mixing of zinc and lead is also recovered. Zinc needs to be separated from lead before being refined [1].

The separation of zinc from lead takes place in a splash condenser in which a molten lead shower enables the lead absorption. The resulting alloy is then cooled and zinc is recovered floating on the surface. It is then refined.

In the **direct smelting** process, lead concentrates and other material are directly charged into the furnace, melted and oxidised before being refined.

Secondary lead is produced from recycled lead wastes and scraps. Battery is a major source of lead.

Batteries can be crushed and separated into different fractions before going to the furnace. The lead recovery process from automotive batteries starts with the drainage of the acid of the batteries before further processing [10].

Lead contained in other material can be recovered using simple smelting processes [1].

There are 2 refining process for lead: the electrolytic refining and the pyrometallurgical refining.

The electrolytic refining is a high cost process, hence it is used where electricity is cheap (e.g. hydroelectricity).

During the pyrometallurgical refining cells are heated, it enables the removal of the impurities. First copper is removed by mechanical skimming, then arsenic, antimony and tin are removed by oxidation associated with mechanical skimming [1].

The primary zinc obtained during the primary lead production is refined using a **distillation process**. It enables during a first step the separation of zinc and cadmium from lead and during a second step the separation of zinc from cadmium is realised. Finally zinc is treated with sodium to remove arsenic and antimony.

In Europe, primary zinc is marginally produced from the primary lead process (~5%), it is essentially produced from **hydrometallurgical process**. This process is used principally for treating zinc sulphides, but also oxides, carbonates or silicates. It involves first the roasting of materials in fluidised bed roasters, which produces sulphur dioxide and a calcine (zinc oxide). The Zinc calcine is then cooled and leached by sulphuric acid. This process is similar to the copper hydrometallurgical process. The Zinc solution obtained is then purified, refined and sent to the cellhouse. Here zinc is extracted by means electrowinning [6].

Secondary zinc production, when treating metallic scrap, consists in physical separation, melting and other high temperature treatment [1]. End-of-life galvanized products are recycled for steel recovery and zinc oxide reports to fumes (Electric Arc Furnace (EAF)-dust) that are further treated pyrometallurgically (Waelz kilns or other furnaces) to recover a 'Zinc oxide'-rich fraction that is further processed for zinc or zinc oxide recovery [6].

# 7.9.4 BAT, Associated Emission Levels (AEL)

If not stated otherwise, emission levels given in this section are given as daily average based on continuous monitoring and standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas without dilution of the gases with air.

#### SO<sub>2</sub>:

During lead and zinc production process, the sulphur contained in materials is oxidised and sulphur dioxide is emitted. Flue gases need then to be desulphurized. Sulphuric acid plants can be used, where there is no pre-treatment of sulphur compounds, to convert these gases. Depending on the flue gas  $SO_2$  content, a single or double contact sulphuric acid plant is considered as BAT to reduce emission levels. Emissions from refining, material pre-treatment and secondary smelting are reduced with  $SO_2$  scrubber. Wet alkaline scrubber or Alkali semi-dry scrubber and fabric filter is considered BAT [1].

For secondary lead plants furnace feed materials can be desulphurized before smelting to reduce  $SO_2$  emissions and enable the plant to meet its emission limits [6].

The following table gives an overview of achievable SO<sub>2</sub> emissions levels in zinc and lead production.

# Table 7: associated $SO_2$ emission levels with BAT to reduce emissions in lead and zinc industry [1] [11]

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Low SO <sub>2</sub> off-stream gas (< 5 %) Primary roasting, smelting and sintering	Single contact sulphuric acid plant or wet gas sulphuric acid plant.	> 99.1 % (conversion factor
SO <sub>2</sub> -rich off-stream gas (> 5 %) Primary roasting, smelting and sintering	Double contact sulphuric acid plant	99.7 – 99.92 % % (conversion factor)
Pre-treatment, secondary smelting, thermal refining, melting secondary zinc processes and slag fuming [9]	Wet alkali scrubbers Alkali semi-dry scrubber and fabric filter.	< 50-200

## NO<sub>x</sub>:

In zinc and lead production, the roasting and the smelting processes are the main sources of  $NO_x$  emissions. Nitrogen oxides are mainly absorbed in the sulphuric acid produced during the primary roasting, smelting and sintering flue gas treatment. Thus  $NO_x$  emissions are not a major issue. BAT to reduce  $NO_x$  emissions at other process steps are the use of oxy-fuel burners and low  $NO_x$  burners [1].

The following table gives an overview of achievable NO<sub>x</sub> emissions levels in zinc and lead production.

# Table 8: associated $NO_{x}$ emission levels with BAT to reduce emissions in lead and zinc industry $\left[1\right]$

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Lead and zinc production	Low NO <sub>x</sub> burner Oxy-fuel burner	< 100 < 100 - 300

#### Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC):

The roasting and smelting processes are the major point sources of dust emissions for lead and zinc industry. The gases need to be collected and treated to reduce dust emission levels. In these production processes, flue gases are collected, cooled and filtered using ESP and fabric filters to control dust emissions and volatile metals contained in dust. [1]. The preferred technique for dust abatement is the use of a fabric filter or a ceramic filter. Electrostatic precipitators should be used for gases containing too much moist, for hot gases, or when the dust is too sticky. Scrubbers should be used as the temperature or the nature of the gases precludes the use of other techniques, or when gases or acids have to be removed simultaneously with dust.

Emissions associated with the use of BAT to reduce dust emissions are presented in the following table.

This source is not identified as a large emitter of BC according to references [15], [16]. BC emission data are scarce. According to [17], there is no BC emission in other non ferrous metal production.

If present in dust, BC emissions can be removed, at least partially, by the use of the same BAT measures described in table 9 for dust which are also efficient for fine particles.

# Table 9: associated dust emission levels with BAT to reduce emissions in lead and zinc industry [1] [5]

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Roasting and smelting	Fabric filters ESP	Dust: 1 – 5

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# 7.10 Cement production

# 7.10.1 Coverage

The emissions from cement plants which cause the greatest concern are nitrogen oxides  $(NO_x)$  and dust . Sulphur dioxide  $(SO_2)$  emissions, are lower but are also considered in this guidance document. This chapter covers installations for production of cement clinker in rotary kilns with a production capacity exceeding 500 tonnes per day, or in other furnaces with a production capacity exceeding 50 tonnes per day [as it is the BREF document] [12].

# 7.10.2 Emission sources

The cement manufacturing process can be divided in 3 steps. The first step is the calcination, in which calcium carbonate (CaCO<sub>3</sub>) is decomposed to form calcium oxide (CaO) at about 900 °C. The following step is the clinker burning in which calcium oxide reacts with silica, alumina, and ferrous oxides at about 1400 to 1500 °C to form the clinker, which is then cooled. Finally the clinker is ground with gypsum and other additives to produce cement.

The clinkering process groups the calcination step and the clinker burning step. It is the largest source of emissions in terms of  $NO_x$ ,  $SO_2$  and dust emissions. The clinkering process takes place in a kiln. Most of the kilns used are rotary kilns. There are different processes used for the clinker production: the dry process, the semi-dry process, the semi-wet process and the wet process. Preheater or precalciner can be added to the process.

More than 75 % of the European clinker production is carried out with dry processes.

In the clinkering process, the raw meal is fed into the rotary kiln system where it is dried, pre-heated, calcined and sintered to produce cement clinker. The clinker is then cooled and stored before being mixed with gypsum to produce cement. [12].

Different preheating technologies are available for the clinkering process.

- **grate preheater** takes place outside of the kiln. With grate preheater rotary kiln becomes shorter, heat losses are reduced and energy efficiency is increased.
- suspension preheating consists in maintaining the meal in suspension with flue hot gas from the rotary kiln. The considerably larger contact surface enables almost complete heat exchange, at least theoretically,
- **precalcination system** divides the combustion in two points. The first burning occurs in the kiln burning zone and the secondary burning takes place in a special combustion chamber between the rotary kiln and the preheater.

The exhaust gases finally go through different cleaning devices to be dedusted and/or desulphurized. [12].

Cogeneration can now be applied in cement plants. The excess heat from the cement production can be used to generate electrical power [12].

# 7.10.3 BAT, Associated Emission Levels (AEL)

If not stated otherwise, emission levels given in this section are expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 10% oxygen and dry gas.

# SO<sub>2</sub>:

In cement production,  $SO_2$  emissions are mainly influenced by content of volatile sulphur in the raw materials. Thus the main measure to reduce  $SO_2$  emissions is the use of sulphur free fuel or fuel with low sulphur content.  $SO_2$  emissions of cement kiln may be very low without any treatment of waste gases: simply when low sulphur raw material and low sulphur fuels are used [10].

However, different flue gas cleaning systems can be used when initial  $SO_2$  emission levels are not very low.

The addition of absorbents such as slaked lime  $(Ca(OH)_2)$ , quicklime (CaO) or activated fly ash with high CaO content to the flue gas can absorb a portion of the SO<sub>2</sub>, it is BAT. This injection can be carried out under dry or wet form. The use of Ca $(OH)_2$  based absorbents with a high specific surface area and high porosity is recommended. The low reactivity of these absorbents implies to apply a Ca/S molar ratio of between 3 and 6.

Wet scrubbing is BAT for desulphurization. In wet scrubbing technologies, the flue gas is first dedusted then cleaned by an atomized solution of alkali compounds.  $SO_2$  reacts with this solution to form different by-products, which can be upgraded as sulphuric acid, sulphur, gypsum or scrubbing agent. A SO<sub>2</sub> reduction of more than 90 % can be expected.[12]

The BAT AEL can be met by applying absorbent addition or wet scrubber.

Regarding the absorbent addition it should be taken into account that the cost of absorbents implies increasing operational costs for increasing  $SO_2$  concentrations, so that this measure might not be cost effective anymore for initial SO2 emissions levels above 1.200 mg/m<sup>3</sup>.

In cement industry values in the range of 50-400  $mg/Nm^3$  are expected when using adapted technologies. The following table gives an overview of BAT associated SO<sub>2</sub> emission levels for cement manufacturing.

Table 1: BAT Associated SO<sub>2</sub> emission levels to reduce emissions in cement Industry [12]

Parameters	Techniques	Associated emission level with BAT <sup>1</sup> (mg/Nm <sup>3</sup> ) (daily average value)
Sulphur in fuel	Absorbent addition	SO <sub>2</sub> : <50 – <400
	Wet scrubbing system	

<sup>1</sup>these values are daily average values and the range takes into account the sulphur content in the raw material

#### NO<sub>x</sub>:

In cement production, NO<sub>x</sub> emissions are influenced by different parameters: the type of fuel, the type of combustion, the combustion air-ratio and the flame temperature. Thus, to reduce NO<sub>x</sub> emissions, several measures can be taken.

Among primary measures, flame cooling, low NO<sub>x</sub> burners, staged combustion, mid kiln firing and addition of mineralisers to the raw material are the main techniques used in cement plants:

**Flame cooling** can be achieved by an addition of water to the fuel or directly to the flame. It drops the temperature and so limits  $NO_x$  formation.

The addition of mineralisers, such as fluorine, to the raw material enables also the reduction of the sintering zone temperature and thus NO<sub>x</sub> formation.

**Low NO<sub>x</sub> burners** enable to reduce NO<sub>x</sub> emissions during combustion processes. Combustion with low NO<sub>x</sub> burner consists in a cold combustion with an internal or external flue gas recirculation. NO<sub>x</sub> reductions up to 30% are achievable in successful installations and emission levels of 600-1000 mg/Nm<sup>3</sup> have been reported with the use of this technology. Erreur ! Source du renvoi introuvable.[12].

In **staged combustion**; the first combustion stage takes place in the rotary kiln. The second combustion stage is a burner at the kiln inlet; it decomposes nitrogen oxides generated in the first stage. In the third combustion stage the fuel is fed into the calciner with an amount of tertiary air. This system reduces the generation of  $NO_x$  from the fuel, and also decreases the  $NO_x$  coming out of the

kiln. In the fourth and final combustion stage, the remaining tertiary air is fed into the system as 'top air' for residual combustion. Staged firing technology can in general only be used with kilns equipped with a precalciner [12].

**Mid-kiln firing** is applied in long wet or dry kilns. It creates a reducing zone by injecting fuel at an intermediate point in the kiln system. In some installations using this technique,  $NO_x$  reductions of 20 – 40% have been achieved.

Primary measures are efficient nevertheless secondary measures can be used to achieve larger  $NO_x$  emission reductions. Among them, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are the main techniques considered in cement plants [6]. In SNCR, the conversion rate is lower: 10 – 50 % is obtained in cement plants.

In cement industry, the BAT for NO<sub>x</sub> emissions reduction are primary measures combined with staged combustion or a SNCR. Emission values in the range of 200-500 mg/Nm<sup>3</sup> are achievable when using these technologies.

Selective Catalytic Reduction (SCR) is BAT, subject to appropriate catalyst and process developments in the cement industry. Large reduction (85 – 95 %) can be expected. At least 2 suppliers in Europe guarantee emissions in the range of 100-200 mg/Nm<sup>3</sup>, when using this technique. However, investment for this technique is still significantly higher than for SNCR [12].

The following table gives an overview of BAT associated  $NO_x$  emission levels for cement manufacturing [12].

If co-incineration waste is used, the requirements of the Waste Incineration Directive (WID) have to be met [12].

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Preheater kilns	Combination of: primary measures (flame cooling, low NO <sub>x</sub> burner, mid kiln firing, addition of mineralisers), staged combustion (also in	<200 - 450 <sup>1 2</sup>
Lepol and long rotary kilns	combination with a precalciner and the use of optimised fuel mix), SNCR, SCR subject to appropriate catalyst and process development in the cement industry.	400 - 800 <sup>3</sup>

<sup>1</sup>BAT-AEL is 500 mg/Nm<sup>3</sup>, where after primary measures techniques the initial NO<sub>x</sub> level is <1000mg/Nm<sup>3</sup>

<sup>2</sup>Existing kiln system design, fuel mix properties including waste, raw material burnability can influence the ability to be in the range. Levels below 350 mg/Nm<sup>3</sup> are achieved at kilns with favourable conditions. The lower value of 200 mg/Nm<sup>3</sup> has only been reported as monthly average for three plants (easy burning mix used);

<sup>3</sup>Depending on initial levels and ammonia slip.

#### Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC):

In cement production, stack dust emissions come from three main sources; the kiln, the clinker cooler and the cement mills. Diffuse emissions come from handling and storage of materials. The crushing and grinding of raw materials and fuels handling can also be significant.

Cement production is not identified as a large emitter of BC according to references [17], [18] and [20]. However BC emission data are scarce.

Electrostatic precipitators (ESP) and fabric filters are used to control dust emissions in cement production. If BC is present in dust, BAT measures described here after, which are efficient for fine particles, are also efficient for BC.The fabric filter should have multiple compartments which can be

individually isolated in case of bag failure and they should be sufficiently designed to allow adequate performance to be maintained if a compartment is taken off line. As the dust is collected the resistance to the gas flow increases and so does the pressure inside the filter. There should be 'burst bag detectors' on each compartment to indicate the need for maintenance when this happens.

Emissions below 5 mg/m<sup>3</sup> can be achieved by well designed and well maintained fabric filters.

Sufficiently dimensioned electrostatic filters, with both good air conditioning and optimised ESP cleaning regime, can reduce dust emission levels below 10 mg/Nm<sup>3</sup> (daily average value).

Control of CO level is necessary for the use of ESP. Concentration of CO has to be kept below the lower explosive limit to avoid any critical problem.

Roads used by lorries needs to be paved and periodically cleaned to avoid diffuse dust emissions. In addition, spraying water at the installation site is used to avoid dust emissions. Chemical agents can also be added to water to improve the efficiency of the agglomeration of dust. As far as possible, material handling should be conducted in closed area, where air need to be collected and cleaned through fabric filters [12].

In cement industry the BAT for dust emissions reduction are ESP and fabric filters. Concentration values in the range of  $5 - 50 \text{ mg/Nm}^3$  of dust are achieved when using these technologies. With the use of hybrid filters (combination of both FF and ESP), values in the range of  $10 - 30 \text{ mg/Nm}^3$  of dust are achieved. The following table gives an overview of BAT associated dust emission levels for cement manufacturing.

Table 3: BAT Associated dust emission levels to reduce emissions in cement lu	ndustry [4], [12]
	10030 1 1 1 1 1 2 1

Emission source	Techniques	Associated emission level with BAT (mg/Nm³)	
All kiln system Clinker cooler Cement mills	Fabric filters or ESP	<b>Dust</b> : <10 – 20	
Dusty operations <sup>1</sup>	Dry exhaust gas cleaning with a filter	<b>Dust:</b> <10 <sup>2</sup>	

 $^1$  It has be noted that for small sources (<10000  $\mbox{Nm}^3/\mbox{h})$  a priority approach has to be taken into account.

<sup>2</sup>spot measurement, at least half an hour.

# 7.10.4 Emerging techniques

As in cement production, the most concerning emissions are  $NO_x$  emissions, emerging techniques presented are techniques to reduce  $NO_x$ .

Fluidised bed combustion, and staged combustion combined with SNCR are emerging techniques to reduce  $\mbox{NO}_{x}$  emission levels.

Using fluidised bed combustion,  $NO_x$  emissions vary from 115 mg/Nm<sup>3</sup> to 190 mg/Nm<sup>3</sup> when heavy oil is used and from 440 mg/Nm<sup>3</sup> to 515 mg/Nm<sup>3</sup> when pulverised coal is used as fuel.

In theory, the combination of staged combustion and SNCR results in similar performance as SCR technology in terms of  $NO_x$  emission levels.

#### 7.10.5 Cost data for emission reduction techniques

The following tables give an overview of the costs for different abatement techniques in cement industry [12], [2].

Table 4: cost of techniques for controlling NO<sub>x</sub> in cement Industry [12]

		Reduction efficiency	Reported costs <sup>1</sup>	
Technique	Kiln systems applicability		Investment (in 10 <sup>6</sup> euros)	Operating (euros/tonne of clinker)
Flame cooling	All	0-35 %	Up to 0.2	Up to 0.5
Low-NO <sub>x</sub> burner	All	0-35 %	Up to 0.45	0.07
Staged combustion	Precalciner	10-50 %	0.1 – 2	0
	Preheater		1 – 4	0
SNCR	Preheater and Precalciner	30 – 90 %	0.5 – 1.2	0.1 – 1.7
	Grate preheater	35 %	0.5	0.84
SCR <sup>6</sup>	Possibly all	43 – 95 %	2.2 – 4.5	0.33 – 3.0

 $^{1}$  Investment cost and operating cost in, referring to a kiln capacity of 3000 tonne clinker/day and initial emission up to 2000 mg NO $_{\rm M}$ m<sup>3</sup>

6 Costs data based on a kiln capacity of 1500 tonne clinker/day

## Table 5: cost of techniques for controlling SO<sub>2</sub> in cement Industry

			Reported costs	
Technique	Kiln systems applicability	Reduction efficiency	Investment (in 10 <sup>6</sup> euros)	Operating (euros/tonne of clinker)
Absorbent addition	All	60-80 %	0.2 – 0.3	0.1 – 0.4
Wet scrubber	All	> 90 %	5.8 – 23	0.5 – 2
Activated carbon	Dry	up to 95 %	15 <sup>2</sup>	No info.

 $^2$  This cost also includes an SNCR process, referring to a kiln capacity of 2000 tonne clinker/day and initial emission of 50-600 mg SO\_2/m $^3$ 

Table 6: cost of techniques for controllin	g dust emissions in cement Industry [1	2].
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		Costs <sup>1</sup>		
Technique	Applicability	Investment	Operating	
			(euros/tonne of clinker)	
Electrostatic precipitators	All kiln systems clinker coolers cement mills	2.1 - 6.0 0.8 - 1.2 0.8 - 1.2	0.1 – 0.2 0.09 – 0.18 0.09 – 0.18	
Fabric filters	All kiln systems clinker coolers cement mills	2.1 - 6.0 1.0 - 1.4 0.3 - 0.5	0.15 - 0.35 0.1 - 0.15 0.03 - 0.04	

<sup>1</sup> Investment cost and operating cost to reduce the emission to 10-50 mg/m<sup>3</sup>, normally referring to a kiln capacity of 3000 tonne clinker per day and initial emission up to 500 g dust/m<sup>3</sup>

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# 7.11 Lime production

### 7.11.1 Coverage

This category covers the lime production and the use of lime kiln in lime industry. It does not cover the lime kiln integrated in other industrial process such as in paper industry.

The emissions from lime plants which cause greatest concern are dust (TSP) emissions. Lime production process is also a source of nitrogen oxides  $(NO_x)$  and sulphur dioxide  $(SO_2)$  emissions. These emissions mainly arise from the limestone calcining process [7].

# 7.11.2 Emission sources

Lime is produced by a heating process. Calcium or magnesium carbonate is heated to form carbon dioxide and lime. During this process,  $NO_x$ ,  $SO_2$  and dust are emitted.

Different techniques are used for lime production. The choice of the technique depends on the quantity of lime to be produced and the size of the feed stones.

Most of used furnaces are based on either the shaft or the rotary design. All of these designs incorporate the concept of three zones: the **preheating** zone where limestone is heated to 800°C, the **calcining** zone where the combustion takes place and enable the formation of lime at over 900°C, and the **cooling** zone where lime is cooled. The lime which exits from the cooling process is called quicklime (CaO).

Some rotary and fluidised bed kilns, are operated in connection with separate preheaters.

Quicklime from the cooling process is screened and fines particles, less pure, are removed. The screened quicklime is then crushed and classified to control the grading of the products.

Slaked lime can also be produced. It includes hydrated lime, milk of lime and lime putty. Hydrated lime is produced from quicklime using a hydrator. Milk of lime and lime putty are produced by slaking of lime in excess of water. Batch and continuous slakers are used for this operation [7].

# 7.11.3 BAT, Associated Emission Levels (AEL)

If not stated otherwise, emission levels given in this section are expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 11% oxygen and dry gas.

#### SO<sub>2</sub>:

In lime production,  $SO_2$  emissions are influenced by the sulphur content of the fuel used during the combustion process.  $SO_2$  emissions also depend on the design of kiln and the required sulphur content of the lime produced. The main measure to reduce  $SO_2$  emissions is the use of free sulphur fuel or fuel with low sulphur content. There is no secondary measure considered in the current BAT to reduce  $SO_2$  emissions. Absorbent addition techniques are available, but not currently applied.

 $SO_2$  from the flue-gases of kiln firing processes can be reduced by using process optimisation measures/techniques to ensure an efficient absorption of sulphur dioxide, i.e. efficient contact between the kiln gases and the quicklime.

As no BAT emission levels are available,  $T_{e}$  prical SO<sub>2</sub> emissions associated with the use of BAT from lime production are presented in the following table [7].

Table 1: associated SO	emission levels with BAT to reduce emissions in lime Industry [7]	I

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> ) <sup>1,2</sup>
Parallel flow regenerative kiln (PFRK), annular shaft kiln (ASK), mixed feed shat kiln (MFSK), other shaft kiln (OSK) and preheater rotary kiln (PRK)	Combination of: process optimisations to ensure an efficient absorption of SO <sub>2</sub> , use of fuel with	<50 <b></b> 200
Long rotary kiln (LRK)	low sulphur content and using absorbent addition techniques	< 50

<sup>1</sup>The level depends on the initial SO<sub>X</sub> level in the exhaust gas and on the reduction measure technique used

<sup>2</sup> For the production of sintered dolime using the "double pass process". SOx emissions might be higher than the upper end of the range.

#### NO<sub>x</sub>:

In lime production,  $NO_x$  emissions are influenced by different parameters: the type of fuel, the type of combustion, the combustion air-ratio and the flame temperature. Those parameters depend on the quality of lime to be produced and the design of kiln.

Both primary and secondary measures can be used in order to reduce  $\mathsf{NO}_{\mathsf{x}}$  emissions. Primary measures include:

- process optimization: smoothing and optimising the plant operation and/or homogenisation of the fuel and raw material feedings.
- burner design: NO<sub>x</sub> emissions can be minimised by the operation of special low NO<sub>x</sub> burners. These burners are useful for reducing the flame temperature and thus reducing thermal and (to some extent) fuel derived NO<sub>x</sub>. The NO<sub>x</sub> reduction is achieved by supplying rinsing air for lowering the flame temperature or pulsed operation of the burners. Low NO<sub>x</sub> burners are only applied to rotary kilns.

Secondary measure that can be applied is:

selective non catalytic reduction (SNCR): in the selective non-catalytic reduction (SNCR) process, nitrogen oxides (NO + NO<sub>2</sub>) from the flue-gases are removed by selective non-catalytic reduction and converted into nitrogen and water by injecting a reducing agent into the kiln which reacts with the nitrogen oxides. The reactions occur at temperatures of between 850 and 1020 °C, with the optimal range is typically between 900 to 920 °C. In lime manufacturing, SNCR is applicable to preheater rotary kilns (Lepol grate). For vertical kilns, it is technically not yet feasible to carry out an SNCR treatment since the temperature of the flue-gas is far below 200 °C. In long rotary kilns, the application of the SNCR technology is not practical as the zone with the optimal window of temperatures is located within the rotating part of the kiln. Being an emerging technique in the lime industry, SNCR is currently only applied in one plant in Europe.

As no BAT emission levels are available,  $\underline{T}$  typical NO<sub>x</sub> emissions <u>associated with BAT</u> from lime production process are presented in the following table [7].

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Annular shaft kiln (ASK), parallel flow regenerative kiln (PFRK), mixed feed shat kiln (MFSK) and other shaft kiln (OSK).	Combination of: primary techniques (use of fuel with low nitrogen content, process	100 – < 350 <sup>1 2</sup>
Long rotary kiln (LRK) Preheater rotary kiln (PRK)	optimisations, burner design (low NO <sub>X</sub> burners), air staging (PRK)) and SNCR (lepol rotary kiln).	< 200 – < 500 <sup>1 3</sup>

#### Table 2: associated NO<sub>x</sub> emission levels with BAT to reduce emissions in lime Industry [7]

1The higher ranges are related to the production of dolime and hard burned lime.

<sup>2</sup>For LRK and PRK with shaft producing hard burned lime, the upper level is up to 800 mg/Nm<sup>3</sup>.

<sup>3</sup>Where primary measures/techniques are not sufficient and where secondary measures/techniques are not available to reduce NOx emissions to 350 mg/Nm<sup>3</sup>, the upper level is 500 mg/Nm<sup>3</sup>, especially for hard burned lime.

# Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC):

In lime production, the kiln and the post-cooling processes are the main sources of dust emissions. Fugitive emissions from handling and storage of materials are also significant.

Rotary kilns are generally equipped with ESP while shaft kilns and lime grinding plants are equipped with fabric filters to control dust emissions. Fabric filters should be equipped with burst bag detectors to indicate the need for maintenance.

Cyclones can also be used to reduce dust emissions but only as flue gases pre-cleaners. Cyclones are easy to operate and cost effective but do not retain effectively microparticles and not avoid the use of ESP or FF.

Flue gases from lime hydrating can be dedusted using wet scrubbers or fabric filters while flue gases from lime grinding can be dedusted using both cyclones and fabric filters.

Lime production is not identified as a large emitter of BC according to references [11], [10] and [13]. However BC emission data are scarce.

If BC is present in dust, BAT measures described here above, which are efficient for fine particles, are also efficient for BC.

The following table gives an overview of achievable dust emissions levels in lime manufacturing.

#### Table 3: Associated dust emission levels with BAT to reduce emissions in lime Industry [7]

	Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )	
Kilns		ESP	Dust: < 204	
		Fabric filters	Dust: < 10 <sup>4</sup>	
	Ducty encretions <sup>1</sup>	Fabric filter	Dust: <10 <sup>2</sup>	
	Dusty operations <sup>1</sup>	Wet scrubbers (mainly used in hydrating plants)	Dust: $< 10 - 20^2$	

<sup>1</sup>It has be noted that for small sources (<10000 Nm<sup>3</sup>/h) a priority approach has to be taken into account.

<sup>2</sup>Values are given as the average over the sampling period (spots measurements, for at least half an hour)

<sup>3</sup>In exceptional cases where resistivity of dust is high, the BAT AEL could be higher, up to 30 mg/Nm<sup>3</sup>, as the daily average value.

<sup>4</sup> Daily average values.

# 7.11.4 Emerging techniques

Considered emerging reduction techniques in lime production are:

- fluidised bed calcinations to reduce SO<sub>2</sub> and NO<sub>x</sub> emission levels.
- absorbent addition (hydrated lime or sodium bicarbonate) to reduce SO<sub>2</sub> emission levels. This
  process needs an optimised residence time to be effective.
- ceramic filters to reduce dust emission levels. They are not currently used but their ability to reduce dust at high temperature makes this technique available.

# 7.11.5 Cost data for emission reduction techniques

As dust emissions are the emissions which cause the greatest concern, costs of reduction techniques are only presented for dust <u>Errour ! Source du renvoi introuvable.[7], [2][7], [2]</u>. There are three main dedusting techniques used for lime kilns : fabric filters, electrostatic precipitators (ESPs) and wet scrubber.

Investments costs are affected by the size of the filter and the operating conditions. Therefore, a wide variation of investment costs exists. The main cost drivers are investments, maintenance and energy.

The cost of dust reduction techniques are presented in the next table.

Mis en forme : Anglais (États Unis)

Mis en forme : Exposant

Technique Applicability		Emission level		Cost <sup>3</sup>	
roomiquo	rippiloability	mg/m <sup>3 1</sup>	kg/tonne <sup>2</sup>	investment	operating
ESP	All kiln systems, milling plant, subsidiary processes	<10 - <20	0.015 – 0.1	0.6 – 3.9	>1.5
	All kiln systems	<10 – <20	0.015 – 0.15		
Fabric filter	Milling plant, subsidiary processes	<10 - <20	0.015 – 0.05	0.25 – 1.7	>1.5
Wet dust separator	All kiln systems, hydrating plants	10 – 30	0.06 - 0.25	-	-

Table 4: cost of techniques for controlling dust in lime Industry

 $^1$  normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 11%  $O_2,$  except for hydrating plants for which conditions are as emitted.

<sup>2</sup> kg/tonne lime based on 3 700 Nm<sup>3</sup>/tonne of lime for rotary kilns with preheaters, 3 000 Nm<sup>3</sup>/tonne of lime for annular shaft kilns and parallel flow regenerative kilns and 5 000 Nm<sup>3</sup>/tonne for long rotary kilns

<sup>3</sup> investment in 10<sup>6</sup> euros and operating cost in euros/tonne lime, referring to different kiln capacities.

# 7.11.6 References used in chapter 7.11

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[13] EPA – Report to congress on black carbon – March 2012

Mis en forme : Exposant

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# 7.12 Glass production

# 7.12.1 Coverage

The sector of glass production includes installations for the manufacture of glass with a melting capacity exceeding 20 tonnes per day. The production of glass fibres and mineral fibres is dealt with in the chapter "Man-Made Fibres" (7-13) This sector includes the manufacture of flat glass and container glass, as well as the production of special glass (TV screen, lighting), domestic glassware and water glass. The production of flat, container and commodity glass is dominated by large multinational companies, whereas the manufacture of table and decorative ware is mainly composed of small and medium sized enterprises. Unlike the production of technical glass, domestic glass production is characterized by a great diversity of products and processes, including hand forming of glass [1], [1], [2], [3].

### 7.12.2 Emission sources

As glass making is an energy intensive activity, the choice of energy source, heating technique and heat recovery are crucial for the environmental performance of an installation. Natural gas, fuel oil and electricity are the three main energy sources. While in the recent decades, fuel oil has been the predominant fuel for glass making, the use of natural gas is increasing due to the ease of control and reduced emissions of SO<sub>2</sub> and CO<sub>2</sub>, however generally at higher cost. Many furnaces are today equipped to run on both natural gas and fuel oil with a fuel change-over only requiring a change of burners; a mixing of fuel and gas in the same burner is also found. Electricity (resistive heating, where a current is passed through the molten glass) is the third energy source for glass making; it can be used either as the exclusive energy source or in combination with other fuels [1][4].

Manufacturing techniques vary from small electricity heated furnaces to cross-fired regenerative furnaces in the flat glass sector, producing up to 900 tonnes per day [4][4].-The following list contains the main melting techniques for different classes of capacities:

- large capacity (>500 t/d) installations: Almost always cross-fired regenerative furnaces
- medium capacity (100 to 500 t/d) installations: regenerative end-port furnaces are favoured, but cross-fired regenerative, recuperative unit melters and also oxy-fuel and electric melters may be used
- small capacity (25 to 100 t/d) installations: Recuperative unit melters, regenerative end port furnaces, electric melters and oxy-fuel melters are used [1].[1].

**Regenerative furnaces** utilize regenerative systems for heat recovery and usually burners in or below combustion air / waste gas ports. Waste gas heat is used to preheat combustion air by passing the waste gas through a heat absorbing chamber. The furnace fires on one side at a time and after about twenty minutes, the firing is reversed and the combustion air is passed through the previously heated chamber. Preheat temperatures up to 1400°C and very high thermal efficiencies may be reached. Regenerative furnaces are either cross-fired (combustion ports and burners along the sides of the furnace, chambers on either side) for rather large installations or end-fired (burners and chambers on one side).

**Recuperative furnaces** utilize heat exchangers for heat recovery, which continuously preheat the combustion air by the waste gases. Temperatures are limited to around 750°C for metallic recuperators and the specific melting capacity of recuperative furnaces is around 30% lower than for regenerative furnaces. The burners are located along each side of the furnace and fire continuously from both sides. Recuperative furnaces are primarily used when high flexibility of operation is required with minimum initial capital, and when regenerators are not economically viable due to small capacity.

**Oxy fuel melting** involves the replacement of combustion air with oxygen (>90% purity), by which the volume of waste gas is reduced by about two thirds. As the atmospheric nitrogen has not to be heated to the flame temperature, energy savings are possible, as well as reduction of  $NO_X$  formation. This

kind of furnace generally has the same design as unit melters (multiple lateral burners, a single waste gas exhaust port), but does not utilize heat recovery systems to pre-heat the oxygen supply.

**Electric melting** uses a refractory lined box with electrodes inserted either from the top, the sides or, more usually the bottom of the furnace. Energy is provided by resistive heating, as the current passes through the molten glass. The technique is commonly applied in small furnaces (especially for special glass), the upper size limit for the economic viability is determined by the cost of electricity compared to fossil fuels. The replacement of fossil fuels in the furnace eliminates the formation of combustion by-products.

**Combined fossil fuel and electric melting** can be either fossil fuel firing with electrical boost or (less common) predominantly electrical heating with a fossil fuel support.

**Discontinuous batch melting** is used when smaller amounts of glass are required, particularly if the glass formulation changes regularly. Pot furnaces or day tanks are used to melt specific batches of raw material, most of them are below the sector threshold of 20 tonnes/day. A pot furnace uses a lower section to preheat the combustion air and an upper section, which holds the pots, serves as the melting chamber. Day tanks are larger and resemble a conventional furnace, but are refilled with batch each day.

Special melter designs were developed to improve efficiency and environmental performance [1][4].

The major environmental challenges for the glass industry are emissions to air and energy consumption. Glass making is a high temperature, energy intensive activity, resulting in the emission of combustion products and the high temperature oxidation of atmospheric nitrogen, i.e. in particular sulphur dioxide, carbon dioxide, and oxides of nitrogen. Furnace emissions also contain dust, which arises mainly from the volatilisation and subsequent condensation of volatile batch materials[4].

# 7.12.3 BAT, Associated Emission Levels (AEL)

## 7.12.3.1 SO<sub>2</sub>

The main techniques for controlling SO<sub>2</sub> emissions are fuel selection, batch formulation and acid gas scrubbing. For oil-fired processes, the main source of SO<sub>2</sub> is the oxidation of sulphur contained in the fuel. SO<sub>2</sub> emissions from the batch vary depending on the use of mainly sodium sulphate for glass oxidation and in some cases sulphite/sulphide in raw materials, but are lower than those from fuel whenever oil-firing is used. The most obvious way for reducing SO<sub>2</sub> emissions is thus to reduce the sulphur content of the fuel or to switch to gas-firing (essentially sulphur free). While the use of fuel with lower sulphur content does not necessarily lead to higher cost (except higher fuel price), the switch to gas-firing requires different burners and several other modifications. It is considered BAT to use gas or oil with a sulphur level of 1% or lower, burning higher sulphur content fuel may also represent BAT if abatement is used to achieve equivalent emission levels [1].[4], [9].

Concerning emissions from batch materials, sulphates are the main source for conventional glass making, as they are the most widely used fining agents and are also important oxidising agents. In most modern glass furnaces, batch sulphates have been reduced to the minimum practicable level.

Concerning scrubbing, the principles of dry and semi-dry scrubbing are the same: the absorbent is introduced to, and dispersed in the waste gas stream, the absorbents chosen for  $SO_2$  are also effective for other acidic gases. The absorbent can be a dry powder (dry process), a suspension or solution with the water-cooling the gas stream (semi-dry process). The recycling of filter dust (including sulphate waste) is often considered reasonable, when technically applicable. This measure can reduce sulphur overall emissions up to the technically feasible substitution in raw materials by filter dust; external disposal routes for the filter dust may be additionally necessary. Thus site-specific solutions may include a balancing of potentially conflicting waste minimisation and sulphur emissions reduction, a process sulphur balance will be essential in this case.

The majority of installed SO<sub>2</sub> scrubbers operate with dry-lime scrubbing at around 400°C, at this temperature a SO<sub>2</sub> reduction of about 50% can be achieved (higher reduction rates possible for around 200°C and humid atmosphere) <u>[1].[4].</u>[5].

For **container glass**, **flat glass**, **domestic glass and special glass**, secondary abatement for dust with dry or semi-dry acid gas scrubbing where appropriate is considered as BAT. Different values are given for BAT depending on the fuel and (for container glass and flat glass) on the emission reduction priority of the installation, as waste minimisation by filter dust and cullet recycling may lead to higher  $SO_2$  emissions.

For **frits**, BAT for SO<sub>2</sub> is considered to be fuel selection (where practicable) and control of batch composition [1] [4].

Emission source	BAT associated emission levels <sup>1</sup> mgSO <sub>2</sub> /Nm <sup>3</sup> or (kg/tonne)		Comments
	gas-firing	oil-firing	
Container glass with SO <sub>2</sub>	200 – 500	500 – 1200	
reduction as priority	(0.3-0.75)	(0.75-1.8)	

Table 1: SO<sub>2</sub> emission levels associated with BAT for furnaces in glass production [1][4]

	• •	-	
Container glass with SO <sub>2</sub>	200 - 500	500 - 1200	
reduction as priority	(0.3-0.75)	(0.75-1.8)	
Container glass with waste minimisation as priority	< 800 (1.2)	< 1500 (2.25)	Where mass balance does not allow the figures above to be achieved.
Flat glass with SO <sub>2</sub>	200 – 500	500 – 1200	
reduction as priority	(0.5-1.25)	(1.25-3)	
Flat glass with waste minimisation as priority	< 800 (2)	< 1500 (3.75)	Where mass balance does not allow the figures above to be achieved.
Domestic glass	200 – 500 (0.5-1.25)	500 - 1300 (1.25-3.25)	If low sulphate in batch, then <200 for gas-firing. Figures in upper part of ranges relate to dust recycling.
Special glass (including water glass)	200 – 500	500 - 1200	Figures in upper part of ranges relate to dust recycling.
Frits	< 200 (0.1-0.5)	500 - 1000	Oil firing is rare.

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

For combustion gases: dry, 8 % oxygen by volume (continuous melters), 13 % oxygen by volume (discontinuous melters). For oxy-fuel fired systems the expression of the emissions corrected to 8 % oxygen is of little value, and emissions from these systems should be discussed in terms of mass.

## 7.12.3.2 NOx

In glass production, nitrogen oxides are mainly generated as thermal NO<sub>X</sub> caused by high furnace temperatures, as a product from decomposition of compounds in the batch materials, and from the nitrogen contained in the used fuels. Thus several parameters have a significant influence on the NO<sub>X</sub> emission levels: the type and amount of fuel used (natural gas, heavy fuel oil), the furnace type (cross-fired, end-fired furnaces; regenerative, recuperative air preheating), the melting temperature and the type of glass produced [1], [2]. The most appropriate techniques for controlling NO<sub>X</sub> emissions are in general: primary measures, oxy-fuel melting, chemical reduction by fuel, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). When using oxycombustion, special care has to be taken with regard to energy efficiency so as not to reduce the NO<sub>X</sub> emission abatement potential [1],[4], [6].

Primary process modifications are based on the following techniques or combinations: reduction of the air/fuel ratio (near stoichiometric combustion), staged combustion<sup>1</sup>, low NO<sub>X</sub> and sealed burners and fuel change. Further measures include the running of furnaces under slightly reducing conditions and to minimize the combustion air supply. The latter is done in order to enhance energy efficiency and to prevent NO<sub>X</sub> formation. It is generally recommended to maintain 0,7-1 % O<sub>2</sub> in unit melters and 1-2% O<sub>2</sub> in end-port furnaces (measured at combustion chamber exit) and to keep the CO level as low as possible (200-300 to 1000 ppm CO maximum)[8], [9].

Secondary techniques for reducing  $NO_x$  emissions in glass manufacturing should be implemented where primary measures do not achieve necessary  $NO_x$  levels. They include the chemical reduction by fuel, the use of selective catalytic reduction (SCR) and, not widely adopted, the use of selective non-catalytic reduction (SNCR), [9].

For **container glass**, the main techniques likely to be considered BAT are primary measures (combustion modifications), oxy-fuel firing, SNCR or SCR (other techniques that achieve the emission levels may also represent BAT). Technically, low  $NO_x$  levels can be achieved using for example the special melters or electric melting. However, these techniques may only be economically applicable in certain circumstances. More widely applicable but options, which may not represent the most appropriate option in all circumstances are oxy-fuel firing and batch/cullet preheating.

Where these secondary techniques require a delay until the next rebuild, many air fuel fired furnaces are expected to achieve emission levels of 600-850 mg/Nm<sup>3</sup> with primary measures only.

For **flat glass** BAT are primary measures. When other techniques (e.g., SCR,) can be used to achieve the given levels, they can also be considered BAT. Where these techniques require a delay until the next rebuild, many air fuel fired furnaces are expected to achieve emission levels of <850 mg/Nm<sup>3</sup> with combustion modifications only.

For **domestic glass**, BAT statements are more difficult, as in the sector high product quality requirements, lower production volumes and more oxidising conditions (higher levels of nitrate) increase the potential for  $NO_x$  emissions. For smaller installations, electrically heated furnaces are an option and are considered BAT for lead crystal, crystal glass and opal glass.

In the short time, using primary combustion measures, emission reductions of up to 40% compared to the current levels are expected. As a medium term proposal, values in the range of 500-700 mg/Nm<sup>3</sup> are expected using the following measures (or combinations thereof) that are considered BAT: primary measures, oxy-fuel-firing or SCR (if costs are acceptable).

For **special glass**, the BAT values are based primarily on the use of oxy-fuel melting and SNCR or SCR. The sector is very diverse and the appropriate technique will depend on site-specific issues.

For **frits**, BAT is the use of oxy-fuel melting or alternatively the use of air-gas systems and primary or secondary measures that are able to achieve the given levels [1].[4].

<sup>&</sup>lt;sup>1</sup> This measure is expected to be phased out with the installation of new low-NOx burners

Emission source	Combination of control measures	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> (kg/tonne)	Comments		
Flat glass	BAT techniques (see text)	500-700 (1.5-1.75)	Transition until next rebuild or substantial use of nitrate compounds: < 850 (2.2)		
Container glass	BAT techniques (see text)	500-700 (0.5-1.1)	Transition until next rebuild: 500-850 (0.9-1.3)		
Special glass	BAT techniques (see text)	500-700			
	Electrical heating	(0.2-1.0)			
Domestic Glass (Lead crystal, crystal glass, opal	Short term modifications: Air-fuel fired	1000-1500 (2.5-3.5)			
glass)	Medium term limit values: Primary measures, oxy-fuel, SNCR, SCR	500-700 (0.5-1.75)			
	Oxy-fuel melting	(0.5-1.5)			
Frits	Air-gas systems and primary / secondary measures	500-700			

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

For combustion gases: dry, 8 % oxygen by volume (continuous melters), 13 % oxygen by volume (discontinuous melters). For oxy-fuel fired systems the expression of the emissions corrected to 8 % oxygen is of little value, and emissions from these systems should be discussed in terms of mass.

### 7.12.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

Dust is emitted by all sub-sectors of glass manufacturing in different process steps. Dust emissions in glass manufacturing industry stem mainly from furnaces and to a lesser extent from batch mixing (use of powdered, granular, or dusty raw materials) and finishing and blasting of glass products. Dust is emitted by the batch plant as volatile components that evaporate and condensate from the batch and the glass melt (mainly sodium sulphate), by combustion of some fossil fuels, in low quantities by materials transportation, handling, storage, and mixing. Dust emissions depend notably on the type of fuel used, the furnace type, and the type of glass produced. Besides end-of-pipe measures, possibilities to slightly reduce direct dust emissions are: pelleting the glass batch, changing the heating system from oil/gas-firing to electrical heating, charging a larger share of glass returns in the batch, and applying a better selection of raw materials (size distribution) [2].

Dust emissions arising through transportation, storage and mixing are typically coarser than those from the high temperature processes, which are generally <  $1\mu$ m.<sup>2</sup> Emissions from storage can be reduced by using enclosed silos, which are vented to suitable dust abatement equipment. During transportation by above ground conveyors, some type of enclosure to provide wind protection is necessary to prevent substantial material loss. These systems can be designed to enclose the conveyor on all sides. Where pneumatic conveying is used, it is important to provide a sealed system

with a filter to clean the transport air before release. To reduce dust during conveying and "carry-over" of fine particles out of the furnace, a percentage of water can be maintained in the batch, usually 3 - 4 % [2].

During the melting cycle using discontinuous furnaces, the dust emission varies greatly. The dust emissions from crystal glass tanks (<5 kg/tonne melted glass) are higher than from other tanks (<1 kg/tonne melted soda and potash glass). Oxy-fuel burners can reduce waste gas volume and flue dust production by 60%. The most significant means for reducing dust emissions from furnaces is the use of either an electrostatic precipitator or a bag filter system, were appropriate in combination with a dry or semi-dry acid gas scrubbing system. Installation of electrostatic precipitators (ESP) can reduce dust emission level with these techniques is 5-30 mg/Nm<sup>3</sup> (equates to 0.1 kg/tonne of glass melted), based on a typical averaging period between 30 minutes and 24 hours. In some cases, BAT for metal emissions may result in lower emission levels for dust [1].[4], [2].

For **container glass**, **flat glass**, **domestic glass**, **special glass**, **frits** BAT for dust is considered the use of an electrostatic precipitator or bag filter operating, where appropriate, in conjunction with a dry or semi-dry acid gas scrubbing system. The application of BAT for metals may in some cases result in lower emission levels for dust [1], [4].

The production of glass is not identified as a major source of black carbon, according to references [12], [13] and [15]. However BC emission data are scarce. BC emissions are linked to incomplete combustion. This type of situation does not occur in glass production which is a continuous process with high level of energy efficiency. Reference [14] provides an emission factor of 0.06 % of TSP. If BC is present in dust, BAT measures described just above, efficient for fine particles, are also efficient for BC.

Emission source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments
Container glass	5-30 (<0.1)	
Flat glass	5-30 (<0.1)	
Domestic glass	5-30 (<0.1)	
Special glass	5-30	
Frits	5-30 (<0.1)	

Table 3: dust emission levels associated with BAT for furnaces in glass production [1][4]

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

For combustion gases: dry, 8 % oxygen by volume (continuous melters), 13 % oxygen by volume (discontinuous melters). For oxy-fuel fired systems the expression of the emissions corrected to 8 % oxygen is of little value, and emissions from these systems should be discussed in terms of mass.

# 7.12.3.4 VOC

VOC emissions from the production of mineral fibres are subject of the section on "man-made fibres" (chapter 7-13). For other glass manufacturing operations, minor emissions of VOCs could also arise for example from cold coating operations. These emissions are not considered to be very significant and are not discussed further.

#### 7.12.3.5 Cross Media Effects

For all mentioned emission reduction and abatement techniques, the cross-media transfer of pollutants and the full range of environmental effects and improvements should be considered. For example additional energy consumption and increased quantities of waste or wastewater residuals may result from individual efforts for pollutant prevention, reduction, or removal.

For the sector of glass production, the recycling of filter dust (including sulphate waste) may lead to higher  $SO_X$  emissions, thus waste minimisation and sulphur emissions reduction may become conflicting targets (eff.refer to chapter 7.12.3.1).

#### 7.12.4 Emerging techniques

In the medium term, no major breakthroughs in technology are expected. Techniques that are already beyond the state of **emerging technologies**, but which are likely to undergo further development are low  $NO_X$  burner systems, oxy-fuel melting, cullet and batch preheating, developments concerning batch formulations, the integration of frit processes. Innovative long-term techniques still at pilot scale are systems using ceramic filters and catalysts combining in one operation NOx, SOx and Dust removal (CERCAT®) and ESP using charged water droplets (TRI-MER®) [1].[4], [10].

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# 7.12.5 Cost data for emission reduction techniques

Abatement Technique	Capital Costs [k€] @ 100/300/600 [Tonnes/d]	Annual Operating Costs [k€] @ 100/300/600 [Tonnes/d]	Specific cost [€/Tonne molten glass] @ 100/300/600 [Tonnes/d]
SCR	615/1000/1800	64/123/330	4.98/2.83/2.99
SNCR	280/450/1350	28/73/225	2.35/1.49/2.16
LowNOx	100/180/550	21/35/72	1.34/0.72/0.83
Oxy-Fuel	-300/-1350/-4800	190/530/1900	4.06/5.05/5.16
3R incl. Repair etc	- /270/680	- /185/285	2.87/2.28/1.91
3R excluding repair	- /140/260	- /106/267	2.20/1.35/1.50
SCR+filter	1500/2420/4550	108/200/470	10.2/5.75/5.78
Filter+scrubber	875/1420/2750	53/89/186	5.52/3.01/3.06

Table 4: cost data for different abatement techniques [1].[4]

Values for a capacity of 100 [tonnes/day] Container (11120 m<sup>3</sup> flue/h), 300 [tonnes/day] Container (23000 m<sup>3</sup> flue/h), 600 [tonnes/day] Float (70000 m<sup>3</sup> flue/h)

Table 5: efficiencies of different NO<sub>x</sub> reduction technologies in Glassmaking [5]

	Achieved reduction	Secondary measures	Achieved reduction
Low-NOx burner	40%	3R process	85%
Staged combustion	35%	SCR	>70%
Oxy-fuel firing	<1kg NO <sub>x</sub> /tonne glass	SNCR	Up to 70%

Table 6: specific cost for different combinations of filters (dust) and scrubbers (SO<sub>x</sub>) for glass furnaces [11]

Type of glass	Production (Tons melt per day)	ESP & dry scrubber (CaOH)₂ Filter dust recycle [€/t]	ESP & dry scrubber (CaOH)₂ Filter dust disposal [€/t]	ESP & dry scrubber (NaHC0₃) Filter dust recycle [€/t]	ESP & dry scrubber (NaHC0₃) Filter dust disposal [€/t]	Bag filter & dry scrubber Filter dust recycle [€/t]	Bag filter & dry scrubber Filter dust disposal [€/t]	Bag filter & semi dry scrubber Filter dust recycle [€/t]	Bag filter & semi dry scrubber Filter dust disposal [€/t]	Wet scrubber [€/t]
Float	500	4.8	6.51				6	7-7.35	9.6 (gas)-13 (oil)	
Float	700	4.27	5.87	4.39	7.75	6.98				
Float	900	3.88	5.44					5.82	8.33	
Container	100-150	11	14							
Container	200		6.7			4.63-5.9	4.8-7			
Container (oil)	200					6.4	9.25			
Container (oil)	300-350	4.52-6	6.31-7.5		7.38-8.33	3.86-5	4.11-7.3	5.3	6.54	
Container	450	3.96-5.2	4.77-6.5			2.9	3.6			
Container (oil)	600	3.58	5.1			2.7	3.37			
Container (gas)	740	4	5.1							
Container (gas)	1240	3.4	4.6							
Container (oil)	1240	3.7	6.2							
Tableware	30-35	15.65	16.7			12.85	13.84			
Tableware	180-200		7.66			3.75-4.35				
E-glass oxy	100-120						11			14.4-21.5*
E-glass air	100-120									15.7-20.5*

Table 7: specific cost for different DeNOx methods for glass furnaces [11]

Type of glass	Production (Tons melt per day)	SCR [€/t]	3R [€/t]	SNCR (recuperative) [€/t]	Basic Lownox measures** [€/t]	Extended Lownox measures*** [€/t]	All-Oxygen firing (€/Nm³) with silica crown* [€/t]	All-Oxygen firing (€/Nm³) with fused cast crown* [€/t]
Float	500	3.3	6-6.25		0.85-1.1		6.83 (0.06)	11.35 (0.06)
Float	700	2.6-2.9	5.25-5.6			2.33		
Float	900	2.6			0.58	1.82		
Container	150						3.07 (0.06)	5.28 (0.06)
Container	200-225	2.56	4.5	2.28	0.76	1.63	3.27 (0.06)	5.39 (0.06)
Container	300	2.13	4	1.88	0.59	1.34		
Container	450	1.84			0.47	1.09	5.18 (0.06)	7.16 (0.06)
Container cross-fired	450		3.73		1.02	1.5 estimated		
Tableware (recuperative)	30-35	8					(at 0.10) -4.32	
Tableware (regenerative)	70						(at 0.10) +12.76	
Tableware (regenerative)	100	4.9						
Tableware (regenerative)	150					8 (high E-boost)		
Tableware (regenerative)	190				0.7			
Special glass oxygen fired	250			3.34				
Special glass regenerative fired	700			2.8				
E-glass	100			4.1			6.20 (0.08)	

\*\*\* Extended Lownox measures: basic measures plus modifications burner ports & combustion chamber

#### 7.12.6 References used for chapter 7.12

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- [3] Technical background documents for the actualisation and assessment of UN/ECE protocols related to the abatement of the transboundary Transport of nitrogen oxides from stationary sources, DFIU, 1999.
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- [15] EPA Report to congress on black carbon March 2012

General References:

US Environmental Protection Agency (US EPA). 1995. "AP-42 Section 11.15, Glass Manufacturing." Washington, DC.

US Environmental Protection Agency (US EPA). Standards of Performance for New Stationary Sources. Subpart CC – Standards of Performance for Glass Manufacturing Plants, 40 CFR Part 60. Washington, DC.

US EPA 1995 Glass Manufacturing Point Source Category. Subpart E – Float Glass Manufacturing Subcategory40 CFR Part 426. Washington, DC.

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#### 7.13 Man-made fibres production

#### 7.13.1 Coverage

The sector production of man-made mineral fibres includes installations for the manufacture of continuous filament glass fibre, of mineral wool and of high temperature insulation glass wools with a melting capacity exceeding 20 tonnes per day. Mineral wool refers to glass wool and stone wool insulating materials, i.e., randomly interlaced masses of fibre that are bound by a resin based binder [1], [2].

#### 7.13.2 Emission sources

Several production steps and environmental issues of the sector "production of man-made fibres" are the same as for the sector "glass production", so the following represents additional information to the basic production technologies, BAT etc. of the "glass production" sector.

**Continuous Filament Glass Fibre** is produced using recuperative or oxy-fuel fired furnaces. The glass flows from the furnace to the forehearths where is passes through bushings on the base. The glass is drawn through the brushing tips to form continuous filaments. The filaments are drawn together and pass over a roller or belt, which applies an aqueous coating to each filament. The coated filaments are gathered together into bundles (strands) for further processing.

**Glass wool** furnaces are usually electric melters, gas fired recuperative furnaces, or oxy-fuel furnaces. Glass flows along a forehearth and through single orifice bushings into rotary centrifugal spinners. Fiberising is by centrifugal action with attenuation by hot flame gases. An aqueous phenolic resin solution is sprayed onto the fibres. The resin-coated fibre is drawn under suction onto a moving conveyor and then passes through an oven to dry and cure the product.

**Stone wool** is usually produced with a coke fired hot blast cupola. The molten material gathers in the bottom of the furnace and flows out along the spinning machine. Air is used to attenuate the fibres and to direct them onto the collection belts. An aqueous phenolic resin solution is prayed onto the fibres by a series of spray nozzles. The remainder of the process is essentially as for glass wool.

**Ceramic fibre** is produced using electric furnaces. The melt is fiberised either by high-speed wheels or high pressure air jet, and the fibres are drawn onto a collection belt. The product can either be baled at this point or processed into blanket to be baled as product or needle felted.

#### Mineral wool

In the mineral wool sector, mainly recuperative and electrical furnaces are used, beside also oxy-gasfired furnaces for glass wool production.

As in the glass industry, the main environmental issues are emissions to air (fossil fuelled furnaces and high-temperature oxidation of atmospheric nitrogen lead to emissions of  $SO_2$ ,  $NO_x$ ,  $CO_2$  and Dust) and energy consumption.

In addition to the emissions found in the glass manufacturing sector, two further important emission sources exist: the forming area (application of binder to the fibres) and the curing oven (drying and curing of binder). In the forming area, dust, phenol, formaldehyde and ammonia are emitted, in the curing oven volatile binder components, breakdown products and combustion products are emitted.

For the production of high temperature insulation glass wools, only electrically heated furnaces are used. Thus only dust emissions are relevant and to a minor extent some organic compounds [1], [2].

#### 7.13.3 BAT, Associated Emission Levels (AEL)

#### 7.13.3.1 SO<sub>2</sub>

In **stone wool production**, important sources of  $SO_2$  emissions (in addition to coke) are the use of blast furnace slag and cement bond briquettes in the batch. The availability of low sulphur coke and slag are restricted by the limited supply within economical transport distances. Slag can normally be eliminated from most batches (except for examples white fibre for specific applications). Using cement bond waste briquettes involves a balance between waste minimisation and  $SO_2$  emission reduction [2].

For **continuous filament glass fibres**, BAT is considered to be the use of secondary abatement for dust with dry or semi-dry acid gas scrubbing where appropriate. The upper parts of the range correspond to dust recycling (otherwise lower values are expected) [2].

For **glass wool** production,  $SO_2$  emissions are often low without any specific abatement equipment, as almost all furnaces are electrically or gas heated and very low levels of sulphate are used. If oil-fired furnaces are used, acid gas scrubbing will usually be necessary to protect dust abatement equipment [2].

For **stone wool** production, the given BAT values correspond to a situation, where priority is given to the recycling of process wastes. Where these values are not reached, acid gas scrubbing may represent BAT (dry scrubbing likely to be most cost effective) [2].

Emission source	BAT associated e mg/Nm <sup>3</sup> (kg/tonne		Comments
	gas-firing oil-firing		
Continuous filament glass fibre	< 200; (0.9)	500 – 1000 (2.25-4.5)	If sulphates in batch, gas-firing <u>values</u> could be up to 800 <u>mg/Nm<sup>3</sup> (3.6</u> <u>kg/tonne</u> ). For oil-firing, upper end of range relates to dust recycling.
Glass wool	generally < 50 (0.1)	300 – 1000 (0.6-2.0)	Generally low sulphate glass.
Stone wool (coke fired) with waste minimisation and recycling as priority.	< 600 < 1100 < 1400	(2.7)	<ul><li>(a) Stone charge</li><li>(b) 45 % cement bound briquettes</li><li>(c) Cement briquettes inc. filter dust</li></ul>
Stone wool (coke fired) with $SO_2$ reduction as priority.	< 200 (0.5) < 350 (0.8) < 400 (1.0)		<ul><li>(a) Stone charge</li><li>(b) 45 % cement bound briquettes</li><li>(c) Cement briquettes inc. filter dust</li></ul>
Ceramic fibre (electric melting)	< 0.5 kg/tonne melt		Electric furnaces only, concentration will be case specific.

Table 1: SO<sub>2</sub> emission levels associated with BAT for furnaces in fibres production [2]

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.<sup>^</sup>

For combustion gases: dry, 8 % oxygen by volume (continuous melters), 13 % oxygen by volume (discontinuous melters). For oxy-fuel fired systems the expression of the emissions corrected to 8 % oxygen is of little value, and emissions from these systems should be discussed in terms of mass.

#### 7.13.3.2 NOx

For **continuous filament glass fibres**, BAT is considered likely to be oxy-fuel melting, however this is no firm conclusion. SCR is considered unlikely to be applicable in the near future due to fears of borate condensation in the catalyst. When using oxycombustion, special care has to be taken with regard to energy efficiency so as not to reduce the  $NO_X$  emission abatement potential.

For **glass wool production**, BAT for NO<sub>x</sub> is considered to be oxy-firing or predominantly electrical melting, conventional firing combined with primary or secondary measures may also be judged BAT if emissions within the ranges are achieved.

Stone wool cupolas do not generally give rise to substantial  $NO_X$  emissions, however where tank furnaces are used, the  $NO_X$  BAT levels correspond to the one of glass wool production [2].

Table 2: NO<sub>x</sub> emission levels associated with BAT for furnaces in fibres production [2]

Emission source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments
Continuous filament glass fibre, oxycombustion	(0.5-1.5)	
Continuous filament glass fibre, other than oxycombustion	500-700	Sector in a transition period concerning $NO_X$ control, emissions generally higher than 1000 mg/Nm <sup>3</sup> (4.5 kg/tonne), with conventional combustion 800 mg/Nm <sup>3</sup> (3.6 kg/tonne) possible
Glass wool	500-700	
	(0.5-1.4)	
Stone wool	(0.5)	For tank furnaces: see level for glass wool
Ceramic fibre	(<0.1-0.5)	

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

For combustion gases: dry, 8 % oxygen by volume (continuous melters), 13 % oxygen by volume (discontinuous melters). For oxy-fuel fired systems the expression of the emissions corrected to 8 % oxygen is of little value, and emissions from these systems should be discussed in terms of mass.

#### 7.13.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

Many statements from the section on glass manufacturing <u>(chapter 7.12)</u> can be transferred to the production of man-made fibres, for example that oxy-fuel burners can reduce waste gas volume and flue dust production by 60%. End-of-pipe prevention and control techniques to reduce dust emission commonly include the installation of electrostatic precipitators (ESP) reducing the emissions to 30 mg/m<sup>3</sup> and fabric (baghouse) filters reducing the emissions below 10 mg/m<sup>3</sup> [1].

For **continuous filament glass fibres**, BAT for dust is the use of an electrostatic precipitator or bag filter operating, where appropriate, in conjunction with a dry or semi-dry acid gas scrubbing system. For this sector, cooling the waste gas and the positioning of the abatement system are very important for optimising efficiency. If existing equipment can achieve emission levels of 50 mg/Nm<sup>3</sup>, costs of replacement prior to the next rebuild could be disproportionate to the advantages gained [2].

For **mineral wool (glass and stone wool)** production, the use of an electrostatic precipitator or bag filter is considered BAT, while acid gas scrubbing systems are not considered necessary due to prevalence of electric or gas heating). For downstream processes, the use of either a wet electrostatic scrubber, a packed bed scrubber, or a stone wool filter (stone wool processes only) is considered BAT.

In the **glass wool production**, the cooling of the waste gas and the positioning of the abatement system are very important for optimising the efficiency. If existing equipment can achieve emission levels of 50 mg/Nm<sup>3</sup>, costs of replacement prior to the next rebuild could be disproportionate to the advantages gained.

For ceramic fibre production, electric melting with a bag filter system is considered BAT [1].

The production of man made fibers is not identified as a major source ob black carbon, according to references [4], [5] and [6]. However BC emission data are scarce. If BC is present in dust, BAT measures described just above efficient for fine particles, are also efficient for BC.

#### Table 3: dust emission levels associated with BAT for furnaces in fibres production [2]

Emission source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments
Continuous filament glass fibre	5-30; (<0.14)	Electrostatic precipitator or bag filter (plus dry or semi-dry acid gas scrubber where appropriate) If existing equipment achieves 50 mg/Nm <sup>3</sup> , costs of major modifications prior to rebuild may be disproportionate
Glass wool		Electrostatic precipitator or bag filter.
Stone wool	5-30 (<0.1)	If existing equipment achieves 50 mg/Nm <sup>3</sup> , costs of major modifications prior to rebuild may be disproportionate
Downstream operations	20-50	combined forming and curing
of mineral wool plants	5-30	curing ovens for stone wool
Ceramic fibres	<10	

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

For combustion gases: dry, 8 % oxygen by volume (continuous melters), 13 % oxygen by volume (discontinuous melters). For oxy-fuel fired systems the expression of the emissions corrected to 8 % oxygen is of little value, and emissions from these systems should be discussed in terms of mass.

#### 7.13.3.4 VOC

In the production of man-made mineral fibres, VOC emissions can be reduced by switching to low organic solvent containing binding agents and/or by VOC adsorption and incineration.

For **stone wool** processes, BAT is considered the use of a thermal incineration unit to reduce curing oven emissions.

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<u>Table 4</u>

Table 4 shows emission levels achievable by switching from conventional to reformulated binding agents and by destructing the emissions generated in the forming and the curing steps (catalytic incineration or adsorption preceded by precipitation of dust) [1].

#### Table 4: VOC emission levels associated with BAT for fibres production [2]

Emission Source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup> or (kg/tonne)	Comments
Glass wool	10-50 [Erreur ! Signet non défini.] (0.12) [1]	forming area and combined forming and curing emissions
Stone wool	< 10	curing ovens: Thermal incineration unit considered BAT
Ceramic fibre	10-20	
load situation. For peak		erage, standard conditions and represents a typical as well as for operational problems of the flue gas er, have to be regarded.

#### 7.13.3.5 Cross Media Effects

For all mentioned emission reduction and abatement techniques, the cross-media transfer of pollutants and the full range of environmental effects and improvements should be considered. For example additional energy consumption and increased quantities of waste or wastewater residuals may result from individual efforts for pollutant prevention, reduction, or removal.

# 7.13.4 Emerging techniques

An emerging technology is the Plasma Melter, which makes use of the electrical conductivity of molten glass and operates with negligible dust emissions. It is however not expected to be a viable technique for melting within the foreseeable future.

# 7.13.5 Cost data for emission reduction technologies

For general cost data for abatement techniques see section 7-12 (glass production).

Table 5: cost data for abatement techniques (only fibres production) [1]

Abatement Technique		Typical Flow Rate Nm³/h	NO <sub>X</sub> mg/Nm <sup>3</sup> or (kg/tonne)	Dust mg/Nm <sup>3</sup> or (kg/tonne)	VOC mg/Nm <sup>3</sup> or (kg/tonne)	Investment for new process M€	Investment for existing process M€	Operating Cost M€/y
Impact scrubber - cyclone	+	150000- 300000		50 (1.8)	30 (1.8)	1.3 <u>+</u> 30 %	1.6 <u>+</u> 40 %	0.1 <u>+</u> 0.02
Impact scrubber - cyclone +WEP	+	150000- 300000		20 (1.2)	30 (1.8)	3.8 <u>+</u> 30 %	4.6 <u>+</u> 40 %	0.12 <u>+</u> 0.02
Impact scrubber -	+	150000- 300000		50 (1.8)	25 (1.8)	3.5 <u>+</u> 30 %	4.2 <u>+</u> 40 %	0.21 <u>+</u> 0.02

cyclone +PBS							
Stone wool slab filter	150000- 250000		20 (0.7)	25 (1.0)	1.3 <u>+</u> 30 %	1.5 <u>+</u> 30 %	0.2 <u>+</u> 0.1
Incinerator	150000- 300000	200 (0.6)	20 (0.1)	10 (0.04)	1.3 <u>+</u> 40 %	1.6 <u>+</u> 30 %	0.2 <u>+</u> 0.1
Stack	150000- 300000				0.7 <u>+</u> 40 %	0.8 <u>+</u> 40 %	

#### 7.13.6 References used in chapter 7.13

- UNECE 2006. Draft background document: Assessment of technological developments: Best Available Techniques (BAT) and limit values. Submitted to the Task Force on Heavy Metals of UNECE CLTRAP
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US EPA. 1995 .Glass Manufacturing Point Source Category. Subpart E – Float Glass Manufacturing Subcategory40 CFR Part 426. Washington, DC.

Technical background documents for the actualisation and assessment of UN/ECE protocols related to the abatement of the transboundary Transport of nitrogen oxides from stationary sources, DFIU, 1999.

# 7.14 Ceramics

#### 7.14.1 Coverage

The sector addresses industrial installations for the manufacture of ceramic products by firing, in particular roofing tiles, bricks, refractory bricks, tiles, stoneware or porcelain, with a production capacity exceeding 75 tonnes per day and/or with a kiln capacity exceeding 4 m<sup>3</sup> and with a setting density per kiln exceeding 300 kg/m<sup>3</sup> [1].

#### 7.14.2 Emission sources

The manufacture of ceramic products takes place in different types of kilns, with a wide range of raw materials. The general process of manufacturing ceramic products, however, is rather uniform except that for some products a multistage firing process is used [1].

The main process steps are:

- raw material preparation and component mixing
- forming and shaping of ware, decoration
- drying ware
- firing ware
- product finishing
- addition of auxiliary materials [2]

In general, raw materials are mixed and cast, pressed or extruded into shape. The water used for a thorough mixing and shaping is evaporated in dryers and the products are placed either by hand in the kiln (especially for periodically operated shuttle kilns) or placed onto carriages that are transferred through continuously operated tunnel or roller hearth kilns. For the manufacture of expanded clay aggregates, rotary kilns are used. During firing, a very accurate temperature gradient is necessary to ensure that the products obtain the right treatment. Today natural gas, liquefied petroleum gas and light fuel oil are mainly used for firing, while heavy fuel oil, liquefied natural gas, biogas/biomass electricity and solid fuels can also play a role as energy source for burners. The main environmental issues are emissions to air as dust and gaseous emissions (carbon oxides, nitrogen oxides, sulphur oxides and others) [1], [3].

# 7.14.3 BAT, Associated Emission Levels (AEL)

For all following pollutants, reductions can be achieved by reducing the energy consumption. In order to achieve this, it is BAT to apply a combination of the following techniques:

- improved design of kilns and dryers
- recovery of excess heat from kilns, especially from their cooling zone
- applying a fuel switch in the kiln firing process (substitution of heavy fuel oil and solid fuels)
- modification of ceramic bodies

It is furthermore considered BAT to reduce primary energy consumption by applying cogeneration on the basis of useful heat demand, within energy regulatory schemes, which are economically viable [1].

#### 7.14.3.1 SO<sub>2</sub>

The emissions of SO<sub>2</sub> in ceramic kiln exhaust gas depend on the sulphur content of the fuel and certain raw materials (gypsum, pyrite, etc). The presence of carbonates in raw materials however may reduce sulphur emissions. In general, techniques for reducing SO<sub>2</sub> emissions include the use of low sulphur content fuels (such as natural gas or LPG), of low-sulphur raw materials and low sulphur

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body-additives. Further reductions are possible by optimising the heating process and lowering the firing temperature and the use of dry or wet scrubbers [4].

Table 1: SO<sub>2</sub> emission levels associated with BAT for ceramics production [1]

Emission Source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup>	Comments
	< 500	Sulphur content in raw material <0.25%
Flue gas from kiln firing	500-2000	Sulphur content in raw material >0.25%; the higher level only applies to raw material with an extremely high sulphur content <u>{Comment: IFC guideline gives a general</u> value of 400 for kiln operations at 10% O <sub>2</sub> ]

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded. Reference conditions: Oxygen content 18 %

IFC guideline [4] gives a general value of 400 mg/Nm<sup>3</sup> for kiln operations in ceramic tile production at 10% O<sub>2</sub> or 110 mg/Nm<sup>3</sup> at 18% O<sub>2</sub>.

#### 7.14.3.2 NOx

The techniques for reducing emissions of gaseous compounds in ceramics manufacturing can be summarized as reducing the input of pollutant precursors (raw materials and additives) and heating curve optimisation (optimal peak flame temperatures, computerized control of kiln firing).

For expanded clay aggregates, it is BAT to keep the emissions from rotary kiln firing below the given BAT value by applying a combination of primary measures/techniques [1], [4].

Table 2:  $NO_x$  emission levels associated with BAT for flue gas from kiln firing in ceramics production [1]

Emission source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup>	Comments
	< 250	Daily average value stated as NO <sub>2</sub> for kiln gas temperatures below 1300 °C
Flue gas from kiln firing	< 500	Daily average value stated as NO <sub>2</sub> for kiln gas temperatures of 1300 °C or above
		{Comment: IFC guideline gives a general value of 600 for kiln operations at 10% O <sub>2</sub> }
Flue gas from kiln firing (expanded clay aggregates)	< 500	Daily average value

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

Reference conditions: Oxygen content 18 %

IFC guideline [4] gives a general value of 600 mg/Nm<sup>3</sup> for kiln operations in ceramic tile production at 10% O<sub>2</sub> or 164 mg/Nm<sup>3</sup> at 18% O<sub>2</sub>.

#### 7.14.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

#### General BAT

The processing of clay and other ceramic raw materials inevitably leads to dust formation, especially drying, grinding, milling, screening mixing and conveying can all result in the emission of fine dust; the

fuels also contribute to these emissions. While diffuse dust emissions should be minimized by appropriate measures (use of silos for all bulk storage of dusty materials or use of confined storage areas within buildings or use of enclosed containers/packaging), for channelled dust emissions, it is BAT to use fabric filters.

For drying processes, it is BAT to clean the dryer, to avoid the accumulation of dust residues in the dryer and to adopt adequate maintenance protocols.

For kiln firing, it is considered BAT to use low ash fuels, to minimise dust formation caused by the charging of the ware to be fired in the kiln and to use flue-gas cleaning by filters or packed bed absorbers [1], [2].

The production of ceramics is not identified as a major source of black carbon, according to references [6] and [7]. However BC emission data are scarce. As presented in chapter 6.1, BC emissions occur during incomplete combustion phases and during start-up periods. If BC is present in dust, BAT measures described just above, efficient fine particles, are also efficient for BC.

#### Sector specific BAT

For wall and floor tiles, household ceramics, sanitaryware, and technical ceramics, vitrified clay pipes it is considered BAT to reduce channelled dust emissions from spray glazing processes by applying fabric filters or sintered lamellar filters.

For wall and floor tiles, household ceramics, technical ceramics it is BAT to reduce channelled emissions from spray drying processes by applying fabric filters, or alternatively cyclones in combination with wet dust separators for existing installations, if the rinsing water can be reused.

For expanded clay aggregates, it is considered BAT to reduce channelled emissions from hot offgases by applying electrostatic precipitators or wet dust separators.

For wall and floor tiles, it is BAT to reduce dust emissions from flue-gases of kiln firing processes, by applying flue-gas cleaning with a fabric filter [1].

#### Table 3: dust emission levels associated with BAT for ceramics production [1]

Emission source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup>	Comments
General BAT		
Channelled emissions from operations other than drying, spray drying or firing	1-10	Half hourly average value by applying fabric filter; may be higher on specific conditions
Drying processes	1-20	Daily average
Kiln firing	1-20 < 50	Daily average; flue gas cleaning with filter Daily average; flue gas cleaning with cascade-type-packed bed absorbers
Sector specific BAT		
Spray glazing (For wall and floor tiles, household ceramics, sanitaryware, technical ceramics, vitrified clay pipes)	1-10	
Spray drying (For wall and floor tiles, household ceramics, technical ceramics)	1-30 1-50	Half hourly average; fabric filters Cyclones in combination with wet dust separators for existing installations, if the rinsing water can be reused
Expanded clay aggregates	5-50	Daily average
Kiln firing (for wall and floor tiles)	1-5	Daily average

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<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded. Reference conditions: Oxygen content 18 %

#### 7.14.3.4 VOC

Emissions of volatile organic compounds (VOC) result from incomplete combustion and from the organic material in the raw materials (e.g., binders, plasticizers, lubricants).

For bricks and roof tiles, refractory products, technical ceramics, inorganic bonded abrasives it is considered BAT to reduce the emissions of VOCs from the flue-gases of firing processes – with raw gas concentrations of more than 100 to 150 mg/m<sup>3</sup>, depending on the raw gas characteristics, e.g., composition, temperature – to the given BAT value by applying thermal afterburning either in a one or a three chamber thermo-reactor.

For refractory products treated with organic compounds it is BAT to reduce the emissions in low offgas volumes from the treatment with organic compounds by applying activated carbon filters. For high off-gas volumes it is BAT to reduce the emissions of VOCs from the treatment with organic compounds by applying thermal afterburning [1], [5].

Emission source	BAT associated emission levels <sup>1</sup> mg/Nm <sup>3</sup>	Comments
Flue gases of firing processes for bricks and roof tiles, refractory products, technical ceramics, inorganic bonded abrasives	5-20	For raw gas concentrations of more than 100-150 mg/m <sup>3</sup> ; as daily average (total C); by application of afterburning, in a 1 or 3 chamber thermo-reactor
Refractory products	5-20	Thermal afterburning

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

#### 7.14.3.5 Cross Media Effects

For all mentioned emission reduction and abatement techniques, the cross-media transfer of pollutants and the full range of environmental effects and improvements should be considered. For example additional energy consumption and increased quantities of waste or wastewater residuals may result from individual efforts for pollutant prevention, reduction, or removal.

# 7.14.4 Emerging techniques

The use of radiant tube burners (flame place inside a heat resistant tube, still under development) can reduce HF and  $SO_2$  emissions. Microwave assisted firing and microwave dryers aim at shorter firing cycles and less excess heat. Large refractory products can be dried more efficiently by placing steel foils or carbon fibres as the heating element into the refractory mix [1].

# 7.14.5 Cost data for emission reduction technologies

Table 5: cost data for different emission reduction techniques for ceramics production [1]

Cleaning system/type	Field of Application	Absorbent /adsorbent	Common sizes/ flowrates for the ceramic industry (Am3/h) <sup>1</sup>	Rough investment guideline (EUR)	Maintenance (EUR/y)	Sorbent cost (EUR/tonne) (EUR/y)	Operation cost (EUR/t)
Dust abatement							
Fabric filter/bag house	Complete areas in the plant, preparation, conveying, storage, forming area, handing over locations, etc.		900 to 70000	6000 – 150000 (Depending on size and amount of ductwork)			0.03 – 0.1
Central vacuum cleaner	Complete areas in the plant, preparation, conveying, storage, forming area, handing over locations, Kiln cars etc.		900 to 1000	25000 – 65000 (Depending on amount of ductwork/pipes)			
Kiln car cleaning system (In different execution: Fixed nozzle, moving nozzle, lifting and adjusting of the plateau)	Kiln cars		8000 to 30000	40000 –200000 (Depending on size and execution)			
Electrostatic precipitator	Dust abatement for hot and large offgas streams		Up to 100000	1000000 – 3000000			0.1 – 0.2
Inorganic gaseous	compounds abatement						

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Module system	Mainly HF reduction	Ca(OH)2 Honeycomb	Very low flowrates	45000 - 100000	~500	~46000 EUR/yr	
Cascade type packed bed absorber	Mainly HF reduction	CaCO3	2500 to 140000 (no lower or upper limit)	40000 – 500000	~2000	30 – 55 EUR/tonne (delivered) 4000 – 30000	23400 – 4800
			2500 to 140000			EUR/yr 95 – 110 EUR/tonne	
Cascade type packed bed absorber	Mainly HF, HCl and SO <sub>2</sub> reduction	Modified/fabricat ed absorbent	(no lower or upper limit)	40000 – 500000	~2000	(delivered) up to 60000 EUR/yr	
Countercurrent type		CaCO <sub>3</sub>				30 – 55 EUR/tonne	
packed bed absorber/ series modules	Mainly HF, HCl, and $SO_2$ reduction	and modified/ fabricated absorbent	2500 to 140000 (no lower or upper limit)	80000 – 800000	~2500	(delivered) respectively 95 – 110 EUR/tonne	
						(delivered)	
Dry sorption with fabric filter (fly stream system)	Mainly HF, HCI, SO <sub>2</sub> Particulate reduction	Ca(OH) <sub>2</sub> in different qualities	2500 to 140000 (no lower or upper limit)	80000-1000000	~4000	95 – 110 EUR/tonne (delivered) 8000 – 45000 EUR/yr	107500 – 130700
Dry sorption with fabric filter (fly stream system) with conditioning of the reaction product	Mainly HF, HCl, and SO <sub>2</sub> Particulate reduction	Ca(OH) <sub>2</sub> in different qualities (with little water added)	2500 to 140000 (no lower or upper limit)	200000 – 1600000	~6500	95 – 110 EUR/tonne (delivered) 8000 – 45000 EUR/yr	107500 – 130700

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Wet scrubber	Mainly HCI and SO <sub>2</sub> reduction	Alkali water	2500 to 140000 (no lower or upper limit)	400000 – 2000000	up to 8000	95 – 110 EUR/tonne (delivered) 8000 – 45000 EUR/yr +water	
VOC abatement							
Thermal afterburning in a thermoreactor (external)			10000 – 50000	180000 – 420000	500 – 4500		
Internal carbonization gas combustion	VOC reduction			42000 – 300000	500 – 8000		

Note: In the column 'common sizes/flowrates' and in the column 'rough investment guideline' there are ranges. It is reasonable to assume that the small Am<sup>3</sup>/h-figures correspond to the low investment figure in EUR and that the high Am3/h figure corresponds to the high investment figure in EUR. In between the increase is not linear, normally the more Am<sup>3</sup>/h are treated, and the lower the investment per Am<sup>3</sup> is.

<sup>1</sup>) The flowrates are given in 'actual m<sup>3</sup>, (Am<sup>3</sup>, as opposed to normal m<sup>3</sup>, standard condition) because actual flue-gas has to be treated.

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Guidance document on control techniques for emissions of sulphur, NOx, VOCs and dust (including  $PM_{10}$ ,  $PM_{2,5}$  and black carbon) from stationary sources

# 7.14.6 References used in chapter 7.14

- [1] European Commission. 2007: "Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Ceramics Manufacturing Industry." <u>http://eippcb.jrc.es/pages/FActivities.htm</u>
- [2] DEFRA 2007: Sector Guidance Note IPPC SG7 Secretary of State's Guidance for the A2 Ceramics Sector including Heavy Clay, Refractories, Calcining Clay and Whiteware. http://www.defra.gov.uk
- [3] Rentz, O., A. Schmittinger, R. Jochum and F. Schultmann (2002): Exemplarische Untersuchung der praktischen Umsetzung des integrierten Umweltschutzes in der Keramischen Industrie unter Beachtung der IVU-Richtlinie und der Erstellung von BVT-Merkblättern, DFIU-IFARE Karlsruhe, report on behalf of Umweltbundesamt, Germany, 221 pp.
- [4] IFC 2007. International Finance Corporation (World Bank Group): Environmental, Health, and Safety Guidelines for Ceramic Tile and Sanitary Ware Manufacturing
- [5] US Environmental Protection Agency (US EPA). 1995. "AP-42 Section 11.15, Glass Manufacturing." Washington, DC.
- [6] UNEP/WMO Integrated Assessment of Black Carbon and Tropospheric Ozone 2011
- [7] UNECE Ad Hoc Expert Group on Black Carbon Black carbon Report by the Co-Chairs of the Ad Hoc Expert Group on Black Carbon. Executive Body for the Convention on Long-range Transboundary Air Pollution. Twenty-eighth session Geneva, 13–17 December 2010

#### **General References**

US Environmental Protection Agency (US EPA). Standards of Performance for New Stationary Sources. Subpart CC – Standards of Performance for Glass Manufacturing Plants, 40 CFR Part 60. Washington, DC.

US EPA 1995 .Glass Manufacturing Point Source Category. Subpart E – Float Glass Manufacturing Subcategory40 CFR Part 426. Washington, DC.

Beerkens 2007 Evaluation of costs associated with air pollution control for glass melting furnaces – A study to support the revision of the IPPC reference document on best available techniques in the glass manufacturing industry 2008, Ordered by CPIV, Brussels, Belgium.

European Commission. 2007: Proposal for a Directive of the European Parliament and of the Council on Industrial Emissions (Integrated Pollution Prevention and Control) (Recast)

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# 7.15 Pulp production<sup>1</sup>

### 7.15.1 Coverage

This chapter covers sulphate (Kraft) and sulphite pulping processes which are the most commonly used processes. Pulp production [5] processes are sources of nitrogen oxides (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>) and dust ( $\frac{TSP_{including} PM_{40}, PM_{2.5}}{TSP_{including} PM_{40}}$ ).

#### 7.15.2 Emission sources

For chemical pulping process as Kraft process and sulphite process, wood is needed. Wood is first debarked and then reduced into chips which are screened. The removed material from the screening operation can be used in the process as solid fuel or be sold for other purposes.

The screened material is then cooked in a cooking plant with different chemical depending on the process. The cooking stage can be continuous or batch.

The sulphate or Kraft process is the most used pulping process, due to the quality of the produced pulp and to its applicability to all wood species.

During the cooking stage of the Kraft process, fibres are liberated from the screened chips using a solution of white liquor to dissolve the lignin. White liquor is composed of sodium hydroxide and sodium sulphide.

The pulp formed in the cooking plant contains fibres and spent cooking liquor; black liquor. Black liquor is removed from the pulp during washing steps and is led to the recovery process. During this recovery process, chemicals and energy are recovered. The recovery system normally enables the whole production process to be self-sufficient in heat and energy.

After the cooking step, delignification can be continued by an oxygen delignification. Then the pulp is purified.

The next step of the process is the bleaching, it is only necessary to obtain brighter Kraft pulp. The bleaching is generally composed of a sequence of separate bleaching stages (4-5). During those stages, chlorine dioxide, oxygen, ozone and peroxide can be used as bleaching agent.

After the bleaching, pulp is purified.

Depending on the type of plant; pulp mill or integrated pulp and paper mill, the final pulp is dried to be transported or directly used as it is [1], [5].

After the cooking step, black liquor is removed and led to a recovery process. To be used as performing fuel, recovered black liquor needs to be concentrated. It is concentrated by evaporation to 65-75% dry-solids content. During the evaporation, non condensable gases and condensates are recovered. Non condensable gases are burnt with malodorous gases while condensates are purified and used as chemicals during the washing of the pulp.

The concentrated black liquor is burnt in a recovery boiler to recover the sodium and sulphur content in a suitable chemical form to regenerate the pulping chemicals and recover energy from the flue gases [1], [5].

The recovery system also enables the regeneration of chemicals; the smelt from recovery boiler are recovered and dissolved in water or white liquor. The solution is then clarified and causticized with lime to form sodium hydroxide, which is then used to produce white liquor.

The calcium carbonate recovered from the causticizing is used in a lime kiln to regenerate lime.

The information included in this subchapter is based on the BREF on pulp and paper industry [1], which is currently under revision at the Institute for Prospective Technological Studies in Sevile (IPTS).

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Air emissions from this process come mainly from recovery boiler, lime kiln, auxiliary boilers and pulp drying.

The recovery boiler is the main source of emissions in the Kraft process. The boiler is fed with concentrated black liquor. NOx,  $SO_{\varrho}$ , and dust emissions occur, and the rate of these emissions are influenced by the combustion efficiency and the sulphur content of the black liquor. The **recovery boiler** is however the main source of emissions in the Kraft process. The boiler is fed with concentrated black liquor, which is the cause of NO<sub>x</sub>,  $SO_{\varrho}$  and dust emissions. These emissions are influenced by the efficiency of the combustion and the sulphur content of the black liquor.

The lime kiln is also responsible of similar emissions as in lime production (refer to chapter 7.11.2).

A bark boiler and other boilers are used in the Kraft process as auxiliary boilers to cover the energy demand of the pulp production. These boilers can be fed with solid, liquid or gaseous fuel [1].

The sulphite process is less used than the Kraft process, due to the lower quality of the produced pulp and to its non applicability to certain wood species. Environmental issues are in most cases more expensive to solve than in the Kraft process.

In the sulphite process, the same processes are used, only the chemicals used are different. Hence, recovering and regenerating steps are slightly different.

The white liquor used in the cooking plant is composed of magnesium sulphite and magnesium bisulphite. The cooking step is most of the time a batch process.

As in the Kraft process, chemicals and energy are recovered to enable the whole production process to be self-sufficient in heat and energy.

Air emissions from this process come from the same sources as in the Kraft process and recovery boiler is also the main source of emissions [1].

#### 7.15.3 BAT, Associated Emission Levels (AEL)

If not stated otherwise the data refer to yearly average values, standard conditions and the reference oxygen content is:

- 6% with solid fuel or biofuel;
- 3% with liquid fuel or gaseous fuel

# SO<sub>2</sub>:

#### Kraft process

The recovery boiler is the major source of  $SO_2$  emissions. Therefore BAT to reduce  $SO_2$  emission levels in pulp industry is first of all reducing emissions from this boiler.

Malodorous gases from cooking plant, delignification step or evaporation of the black liquor need to be collected and incinerated in the lime kiln, the recovery boiler or the auxiliary boilers. Emissions from incineration need to be controlled.

In the recovery boiler, the use of high dry solids content of black liquor is a primary measure to reduce  $SO_2$  emissions. A high dry solid content >75% permits to reduce significantly emissions.

In order to reduce SO<sub>2</sub> emissions from the recovery boiler, a flue gas wet scrubber can be installed as secondary measures. The scrubbing enables the removal of SO<sub>2</sub> and dust. The pH is controlled and regulated by addition of liquor or sodium hydroxide. SO<sub>2</sub> reacts with the scrubbing liquor to form sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>) or sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>). The usual removal efficiency of this scrubbing is > 90 %. From initial concentration levels of 50-200 mg/Mm<sup>3</sup>, levels of 10-50 mg/m<sup>3</sup> can be reached.

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The reduction of SO<sub>2</sub> emissions from other boilers involves the use of low sulphur content fuels or the use of scrubber to control emissions [1].

The following table gives an overview of BAT associated SO<sub>2</sub> emission levels for Kraft pulping process using different techniques.

Table 1: associated SO <sub>2</sub> emission levels with BAT to reduce emissions in Kraft pulping process	
[1]	

Emission source	Techniques	Associated emission level with BAT (mg S/Nm <sup>3</sup> )
Recovery boiler (5% O <sub>2</sub> )	SO <sub>2</sub> scrubbing system If with High dry solids content of black liquor (>75%)	10 – 50 it goes to 5 – 10
Auxiliary boilers	Use of fuel with low sulphur content	$100 - 200^{1} \\ 25 - 50^{2} \\ <5^{3} \\ <15^{4}$
	SO <sub>2</sub> scrubbing system	50 – 100 <sup>1</sup>

feed with coal or heavy fuel oil

<sup>2</sup> feed with gas oil

<sup>3</sup> feed with gas <sup>4</sup> feed with biofuel

#### Sulphite process

As for Kraft pulping process, the recovery boiler is responsible for the major part of SO2 emissions in the sulphite pulping process.

Similar primary measures can be applied to reduce emissions.

In order to reduce SO<sub>2</sub> emissions from the recovery boiler, a flue gas multi staged scrubber can be used. SO2 emissions from the other boilers can be reduced using the same reduction techniques as for Kraft process.

The following table gives an overview of BAT associated SO2 emission levels for sulphite pulping process using different techniques.

Table 2: associated SO <sub>2</sub> emission levels with BAT to reduce emissions in sulphite pulping
process [1]

Emission source	ource Techniques			
Recovery boiler (5% O <sub>2</sub> )	SO <sub>2</sub> multi-staged scrubber	50 – 150		
Auxiliary boilers	Use of fuel with low sulphur content	$100 - 200^{1} \\ 25 - 50^{2} \\ <5^{3} \\ <15^{4}$		
feed with coal or beavy fuel oil	SO <sub>2</sub> scrubbing system	50 – 100 <sup>1</sup>		

<sup>1</sup> feed with coal or <sup>2</sup> feed with gas oil or heavy fuel oil

<sup>3</sup> feed with gas <sup>4</sup> feed with biofuel

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#### NO<sub>x</sub>:

#### Kraft process

The main sources of NO<sub>x</sub> emissions in the Kraft process are the lime kiln and the recovery boiler. The recovery boiler is responsible for the largest part of NO<sub>x</sub> emission due to the amount of black liquor burnt. Low NO<sub>x</sub> burners and modified combustion conditions with staged air feed system can reduce the emission levels.

The high combustion temperature in the lime kiln is also responsible of NO<sub>x</sub> emissions. The level of emissions is influenced by the type of fuel used. Primary measures such as adjusting functioning parameters like flame shape or air distribution, can control the NO<sub>x</sub> emissions.

Auxiliary boilers within the pulp industry are of a very large range size (from 10 to above 200 MW). Therefore, different measures can be applied from small boiler to large boilers. In smaller boilers, structural and primary measures are cost effective while in larger boilers, secondary measures can also be applied [1].

The following table gives an overview of BAT associated  $NO_{\text{x}}$  emission levels for Kraft pulping process.

#### Table 3: associated NO<sub>x</sub> emission levels with BAT to reduce emissions in Kraft pulping process [1]

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )			
Recovery boiler (5% O <sub>2</sub> )	Low $NO_x$ burner, staged air feed system	80 – 120			
Lime kiln	adjusting parameters : oil firing gas firing	80 – 180 <sup>5</sup> 300 – 540 <sup>5</sup>			
Auxiliary boilers	structural and primary measures	$80 - 110^{1}  45 - 60^{2}  30 - 60^{3}  60 - 100^{4}$			
	SNCR				

feed with coal or heavy fuel oil

<sup>2</sup> feed with gas oil <sup>3</sup> feed with gas <sup>4</sup> feed with biofuel

+<sup>5</sup> AEL exactly reproduced from the BREF [1]. However 300-540 should refer to oil firing and 80-180 to gas firing. As written in the Bref document, it could be an error]

#### Sulphite process

The main sources of  $NO_x$  emissions in the sulphite process are the boilers. Hence,  $NO_x$  emissions from those boilers can also be reduced using the same reduction techniques as for Kraft process.

The following table gives an overview of BAT associated NO<sub>x</sub> emission levels for sulphite pulping process in pulp industry.

#### Table 4: associated NO<sub>x</sub> emission levels with BAT to reduce emissions in sulphite pulping process [1]

Emission source	source Techniques			
Recovery boiler (5% O <sub>2</sub> )	Low $NO_x$ burner, staged air feed system	200 - 300		
Auxiliary boiler	Structural and primary measures	$80 - 110^{1} 45 - 60^{2} 30 - 60^{3} 60 - 100^{4}$		
	SNCR	50 - 80 <sup>1</sup> 40 - 70 <sup>4</sup>		

feed with coal or heavy fuel oil

<sup>2</sup> feed with gas oil <sup>3</sup> feed with gas

4 feed with biofuel

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#### Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC):

#### Kraft process

In kraft pulp mills, dust emissions come from different sources, mainly the lime kiln, the auxiliary boiler and the recovery boiler. Emissions can be controlled by electrostatic precipitator and/or SO<sub>2</sub> scrubbers depending on the emission source process. Bag filters can also be used [7].

The SO<sub>2</sub> scrubbers used on boilers also enable the control of the dust emissions.

For new boilers, only the use of ESP is considered to be BAT to reduce dust emission levels. For existing boilers, the combination of ESP and scrubbers is necessary.  $SO_2$  scrubber combined with an ESP can achieve about 15 mg/Nm<sup>3</sup> of dust emissions.

The following table gives an overview of BAT associated dust emission levels for Kraft pulping process.

Paper pulp production is not identified as a large emitter of BC according to references [9], [10] and [12]. However BC emission data are scarce. If BC is present in dust, BAT measures described just above for dust which are efficient for fine particles, are also efficient for BC.

# Table 5: associated dust emission levels with BAT to reduce emissions in the Kraft pulping process [1], [2]

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )		
Lime kiln	ESP	dust: 30 – 50		
Recovery boilers (5% O <sub>2</sub> )	ESP and SO <sub>2</sub> scrubbers	dust: 30 – 50		
		<sup>1</sup> dust: 10 – 30		
Auxiliary boilers	ESP	ESP <sup>2</sup> dust: 10 – 40		
		<sup>3</sup> dust: < 5		

feed with coal or biofuel or gas oil

<sup>1</sup> feed with heavy fuel oil <sup>3</sup> feed with gas

leed with gas

#### Sulphite process

In sulphite pulp mills, dust emissions come from different sources, mainly the lime kiln, the auxiliary boiler and the recovery boiler. Emissions can be controlled using the same systems as for the Kraft process.

The following table gives an overview of BAT associated dust emission levels for sulphite pulping process.

Paper pulp production is not identified as a large emitter of BC according to references [9], [10] and [12]. However BC emission data are scarce. If BC is present in dust, BAT measures described just above which are efficient for fine particles, are also efficient for BC.

Table 6: associated dust emission levels with BAT to reduce emissions in the sulphite pulping process [1], [2]

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> )
Recovery boilers (5% O <sub>2</sub> )	ESP and SO <sub>2</sub> scrubbers	<b>dust:</b> 5 - 20
		<sup>1</sup> <b>dust:</b> 10 – 30
Auxiliary boilers	ESP	² <b>dust:</b> 10 − 40
		<sup>3</sup> dust: < 5

feed with coal or biofuel

<sup>1</sup> feed with heavy fuel oil

<sup>3</sup> feed with gas

### 7.15.4 Emerging techniques

The installation of SNCR on recovery boilers, main source of  $NO_x$  emissions, is considered as emerging reduction technique in pulp industry, as it is a new application of this common technique.

The investment for a complete installation of SNCR (*NOxOUT* process) on a recovery boiler (black liquor load: 1600 t dry solids/day) is about 2.2 - 2.8 Meuros.

Due to its low rate of use, no emerging techniques are identified for emissions reduction in the sulphite process [1].

#### 7.15.5 Cost data for emission reduction techniques

 $SO_2$  scrubbers on recovery boilers come usually as a package from the supplier. Investment for a bleached Kraft mill with a production capacity of 250,000 and 500,000 t/y amount to 7.2 Meuros and 10.4 Meuros respectively. They include scrubber, scrubber liquor pumps, circulation pumps, electrification and instrumentation. Operating costs amount to 0.58 Meuros/y and 0.92 Meuros/y respectively [1][4].

The investment to add a SNCR process to the bark boiler for the same production capacity plant is about 0.7-1.15 Meuros. The investment costs include injection equipment, pipes, pumps, tanks and rebuild/adoption of the boiler. The operating costs are mainly due to urea consumption, about 1-2 kg urea is required per kg NO<sub>x</sub> removed [1][4].

The installation of electrostatic precipitator costs about 3-4 Meuros for the bark boiler (auxiliary boiler) and 5-6 Meuros for the lime kiln. Operating costs are less than 0.3 Meuros/y in both cases [1][+].

Investments for low NO<sub>x</sub> technology in auxiliary boilers or lime kilns are 0.5 - 0.8 Meuros.

#### 7.15.6 References used in chapter 7.15

- [1] Reference document on Best Available Techniques in the pulp and paper industry, December 2001.
- [2] EPA 42 volume 1 chapter 1, September 1998.
- [3] Auswertung von staub- und Feinstaubemissionsdaten der Datenbank nordrhein-westfälisher Emissionserklärungen, LUA NRW, 2003.
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- [5] Comments from Almut Reichart, UBA, 12/2008
- [6] "Compilation of the answers-to-questions-and proposal of EGTEI secretariat.doc", EGTEI, 02/2009.
- [7] Comments from Thomas Krutzler, UBA Austria, 03/2009.
- [8] "EGTEI-State of progress.doc", for WGSR, March 2009.
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# 7.16 Nitric acid production

#### 7.16.1 Coverage

Nitric acid (HNO<sub>3</sub>) is one of the most produced chemical product. Emissions to the atmosphere from nitric acid production which cause the greatest concern are nitrous oxide (N<sub>2</sub>O) and nitrogen oxides (NO<sub>x</sub>) emissions. The Gothenburg Protocol deals with transboundary air pollution and particularly with acidification and eutrophication. It sets emission ceilings for sulphur, nitrogen oxide, VOC, ammonia and dust but it does not cover N<sub>2</sub>O which is a green house gas with high global warming potential. Hence, this chapter is mainly focused on NO<sub>x</sub> emission reductions.

#### 7.16.2 Emission sources

HNO<sub>3</sub> is produced from ammonia (NH<sub>3</sub>), which is evaporated, filtered and oxidised to form nitric oxide (NO). Ammonia filtration is necessary in order to remove all dust. It avoids interaction between dust particles and catalysts on which ammonia oxidation takes place.

The NO formed during the oxidation is then also oxidised to form nitrogen dioxide (NO<sub>2</sub>). NO<sub>2</sub> is then absorbed in H<sub>2</sub>O to form nitric acid and nitric oxide. The absorption process is an important source of NO<sub>x</sub> emissions; hence NO<sub>x</sub> need to be controlled and reduced. Different techniques are available to reduce these emissions.

#### 7.16.3 BAT, Associated Emission Levels (AEL)

#### **Primary measures**

Major  $NO_x$  emissions come from the step of formation of HNO<sub>3</sub>. One of the different applicable techniques to reduce  $NO_x$  emissions involves the optimisation of the absorption stage. The more the absorption is efficient, the more HNO<sub>3</sub> is formed and the less  $NO_x$  is emitted [1].

The efficiency increase of this absorption is based on the optimization of 3 parameters; the temperature, the pressure and the contact between  $NO_x$ ,  $O_2$  and  $H_2O$ .

- due to the reaction exothermia, heat removal is needed to optimise the temperature process. The absorption stage takes place in the first third of the column, thus heat removal can be applied before the column.
- high pressure increases the efficiency of the absorption and then nitric acid formation. It also reduces the formation of NO<sub>x.</sub>
- optimising the contact in the absorption tower mainly means changing the tower design. The volume, the number of trays and the residence time are the main parameters to play with so as to optimise the absorption. The longer the residence time is, the more NO<sub>x</sub> is recovered and the more nitric acid is formed. The increase of the number of trays and of the volume enhances the nitric acid formation too.

Tail gas concentration level of  $82 - 103 \text{ mg/Nm}^3$  is technically feasible with completely optimised absorption (heat removal, high pressure, optimised contact).

The  $HNO_3$  yield can also be increased by addition of  $H_2O_2$  to the last absorption stage. It avoids the implementation of a SCR\_[1].

#### Secondary measures

 $NO_x$  emissions can be reduced by a tail gas treatment, such as a combined  $N_2O$  and  $NO_x$  abatement technique or a SCR can also be used.

The combined N<sub>2</sub>O and NO<sub>x</sub> abatement technique consists of 2 catalyst layers. In the first layer, N<sub>2</sub>O is reduced in N<sub>2</sub> and O<sub>2</sub>. In the second layer, NO<sub>x</sub> is reduced by addition of NH<sub>3</sub> (comparable to a SCR) and N<sub>2</sub>O further decomposition is also taking place. This process can lead to a NO<sub>x</sub> abatement of 99 %.The process is applicable for nitric acid plants with a tail gas temperature of more than 400 degree Celsius [1].

For installations with a tail gas temperature of more than 340 degree Celsius N<sub>2</sub>O and NOx emissions can be reduced in a combined N<sub>2</sub>O and NOx abatement system with the addition of hydrocarbons- [4]. As in the combined N<sub>2</sub>O and NO<sub>x</sub> abatement process, there are 2 catalyst layers. In the first one, NO<sub>x</sub> is removed in reacting with NH<sub>3</sub> and N<sub>2</sub>O is removed by a catalytic reduction with hydrocarbon (natural gas or propane) in the second step. Similar emission levels as in the N<sub>2</sub>O and NO<sub>x</sub> combined abatement technique can be expected- [1].

The following table gives an overview of BAT associated  $NO_x$  emission levels for nitric acid production.

Table 1: associated  $\mbox{NO}_{\mbox{x}}$  emission levels with BAT to reduce emissions in nitric acid production.

Emission source	Emission source Techniques	
Nitric acid production	Optimisation of the absorption stage, Combined NO <sub>x</sub> and N <sub>2</sub> O abatement technique , SCR, Addition of $H_2O_2$ to the last absorption stage	New plants 10 - 154 Existing plants 10 – 185 <sup>2</sup>

<sup>1</sup>emissions were converted from ppmv to mg / Nm<sup>3</sup> using: 1ppmv = 2.05 mg NO<sub>2</sub> / Nm<sup>3</sup>.

 $^2$  up to 307 mg/Nm $^3$ , where safety aspects due to deposits of AN restrict the effect of SCR or with addition of H<sub>2</sub>O<sub>2</sub> instead of applying SCR.

#### 7.16.4 Emerging techniques

There is no emerging technique available to reduce NOx emissions in HNO<sub>3</sub> production [1].

#### 7.16.5 Cost data for emission reduction techniques

The investment of a combined N<sub>2</sub>O and NO<sub>x</sub> treatment unit is about 1.7 Meuros. A comparison of various N<sub>2</sub>O reduction strategies does not show a significant difference in cost effectiveness and the cost per tonne HNO<sub>3</sub>. Operating costs are between 0.71-0.87 euros per tonne  $CO_2$ -eq reduced and 0.98 – 1.20 euros per tonne HNO<sub>3</sub> produced.

There is no available information about the cost of the hydrocarbon addition technique.

The total cost for a SCR technique is around 1.3 USD per tonne HNO<sub>3</sub> produced. This estimation was made in 1998 assuming certain price of catalyst and fuel, which are now significantly different  $\tau_{\tau}$ [1].

The specific cost of the implementation of the addition of  $H_2O_2$  to the last absorption stage is 2.5 USD per tonne HNO<sub>3</sub>.

#### 7.16.6 References used in chapter 7.16

- [1] Reference document on Best Available Techniques for the manufactures of large volume chemicals ammonia, acids and fertilizers, August 2007.
- [2] Comments from Birgit Brahner, German Federal Environment Agency, 12/2008.
- [3] "Compilation of the answers-to-questions-and proposal of EGTEI secretariat.doc",EGTEI, 02/2009.
- [4] Comments from Thomas Krutzler, UBA Austria, March 2009.
- [5] EGTEI-State of progress.doc", for WGSR, March 2009.

# 7.17 Sulphuric acid production<sup>1</sup>

### 7.17.1 Coverage

The production of sulphuric acid ( $H_2SO_4$ ) is in terms of quantities the most important production of the industrial chemical production. The production of  $H_2SO_4$  varies from the SO<sub>2</sub> sources.

The emissions to the atmosphere from sulphuric acid production which cause greatest concern are sulphur dioxide (SO<sub>2</sub>) emissions. This chapter covers the chemical production of sulphuric acid.

# 7.17.2 Emission sources

 $H_2SO_4$  is produced from sulphur dioxide or elemental sulphur. Elemental sulphur is derived from desulphurisation of natural gas or crude oil.  $SO_2$  is derived from flue gas process, e.g.  $SO_2$  gases from sulphur, the roasting of zinc and /or lead minerals, regeneration of spent acids, non ferrous metal production, or waste gas incineration, etc.

 $SO_2$  is first oxidised on catalysts to  $SO_3$ . Catalysts used are based on vanadium compounds, platinum and iron oxides [6].

 $SO_3$  is then absorbed in  $H_2SO_4$  to form sulphuric acid. High  $SO_2$  emission levels come from this part of the process; hence measures to reduce  $SO_2$  emissions have to be used.

# 7.17.3 BAT, Associated Emission Levels (AEL)

# SO<sub>2</sub>: [1][1]

The major  $SO_2$  emissions come from the absorption process tail gas.  $SO_2$  emissions depend on the conversion rate of the process. Process optimisation can be considered as the best available technique to reduce emissions.

Different techniques to increase  $SO_2$  conversion rate can be combined in order to achieve BAT associated emission levels.

A double contact/double absorption process improves the conversion yield of  $SO_2$  from the tail gas. A change from a single absorption to a double absorption can significantly reduce  $SO_2$  emissions.

The addition of a fifth bed catalyst in the double contact process can increase the conversion rate to 99.9 %. This technique is generally applicable for double contact plants, provided that sufficient room is available [1]. Usually applying double contact process maximum conversion rate is 99.8 % in a steady-state operation, maximum conversion rate 99,6% under transient operation conditions. But this technique's application in an existing plant has two main difficulties: the high cost of the investment and the high cost of the operation, owing to the need of external heating, owing to the difficulty of reaching the proper temperatures for the operation of catalyst and to the fluodynamic characteristics of the installed blowers [6].

The use of a Cs promoted catalyst can also increase the conversion rate of SO<sub>2</sub>. Indeed, Cs promoted catalysts can be used at lower temperature  $(380 - 620^{\circ}C)$  than conventional catalysts  $(420 - 660^{\circ}C)$ .

The replacement of brick-arch converters, too porous, can lead to an increase of SO<sub>2</sub> conversion rate.

The use of wet catalysis process enables the conversion of wet SO<sub>2</sub> gases.

Finally, a regular maintenance of utilities and replacement of catalysts is necessary to maintain a high conversion rate.

<sup>1</sup> The information included in this subchapter is based on the BREF [1] on large volume chemicals. Some new information from the BREF non ferrous metal industry, which is currently under revision at the Institute for Prospective Technological Studies in Seville (IPTS), should be available in a near term.

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Secondary measures can also be applied.

Tail gas can be scrubbed using an aqueous ZnO solution or  $NH_3$  solution, or other alkaline solutions such as sodium hydroxide, as well as hydrogen peroxide. These scrubbing can provide by-products that can be used on-site or sold [4]. <u>Erreur ! Source du renvoi introuvable.</u>

The BAT to reduce  $SO_2$  emissions is a combination of the formerly cited processes and reduction techniques permitting to achieve the emission levels detailed in the following table.

The following table gives an overview of BAT associated  $SO_2$  emission levels for sulphuric acid production.

Table 1: associated  $\mbox{SO}_2$  emission levels with BAT to reduce emissions in sulphuric acid production

Emission source	Techniques	Associated emission level with BAT (mg/Nm <sup>3</sup> ) <sup>1, 2</sup>		
Sulphuric acid production	Sulphur burning, double contact/double absorption	Existing installations : 30-680 New installations : 30-340		
	Other double contact/double absorption	200-680		
	Single contact/single absorption	100-450		
	Other	14-170		

<sup>1</sup> This level might include the effect of tail gas scrubbing.

<sup>2</sup> Expressed as daily average value.

# 7.17.4 Emerging techniques

No data available.

#### 7.17.5 Cost data for emission reduction techniques

The addition of a fifth bed to a double contact process needs an investment of about 1 million euros. The specific cost related to  $SO_2$  reduction is 629 euros per ton  $SO_2$  reduced [1].

The investment cost of the application of promoted-Cs catalyst in a double contact process is 21 700 euro/y more than the original investment for traditional catalyst. The specific cost related to  $SO_2$  reduction is 12 euros per ton  $SO_2$  reduced. This cost increases to 930 euros per ton  $SO_2$  reduced for a single contact process [1].

The following table gives an overview of the costs and  $SO_2$  conversion rate for different abatement techniques in sulphuric acid production [8].

	Capacity (t H₂SO₄/d)	% SO <sub>2</sub>	Construction		SO <sub>2</sub> -Conversion average (%)		Costs €/t SO <sub>2</sub> €/t H <sub>2</sub> SO <sub>4</sub>		SO <sub>2</sub> avoided	Annualised costs	SO <sub>2</sub> unabated
Nr.											
		(t H <sub>2</sub> SO <sub>4</sub> /d) c	content	before	after	before	after	abated	additionaly	(t/year)	(€/year)
			4 bed SC/SA	Base case A1	98.00	-	0	0	0	0	1143
3		-	4 bed SC/SA	+ Cs in bed 4	98.00	99.10	3	0.02	628	1 763	
4		5 - 7	4 bed SC/SA	4 bed DC/DA	98.00	99.60	1 317	13.76	914	1 203 985	
2		5-7	4 bed SC/SA	4 bed DC/DA + Cs in bed 4	98.00	99.70	1 159	12.87	971	1 125 848	
4		-	4 bed SC/SA	+ TGS Peracidox	98.00	99.87	1 048	12.80	1 068	1 119 881	
5	250	ľ	4 bed SC/SA	+ TGS (alkaline)	98.00	99.87	1 286	15.70	1 068	1 373 446	
	-		4 bed DC/DA	Base case A2	99.60	-	0	0	0	0	228
6		9 - 12	4 bed DC/DA	+ Cs in bed 4	99.60	99.70	367	0.24	57	20 858	
7			4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	3 100	4.03	114	352 656	
8		ľ	4 bed DC/DA	+ TGS Peracidox	99.60	99.94	3 910	8.68	194	759 562	
9		ľ	4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	6 636	14.73	194	1 287 390	
			4 bed SC/SA	Base case B1	98.00	-	0	0	0	0	2286
<del>12</del>		ľ	4 bed SC/SA	+ Cs in bed 4	98.00	99.10	5	0.04	1 257	6 285	
<b>10</b>		5 - 7	4 bed SC/SA	4 bed DC/DA	98.00	99.60	867	9.06	1 829	1 584 685	
44			4 bed SC/SA	4 bed DC/DA + Cs in bed 4	98.00	99.70	835	9.27	1 943	1 622 590	
<b>13</b>	500		4 bed SC/SA	+ TGS Peracidox	98.00	99.87	718	8.77	2 137	1 535 220	
44	500	ľ	4 bed SC/SA	+ TGS (alkaline)	98.00	99.87	883	10.78	2 137	1 886 839	
			4 bed DC/DA	Base cas C1	99.60	-	0	0	0	0	457
<del>15</del>		9 - 12	4 bed DC/DA	+ Cs in bed 4	99.60	99.70	363	0.24	114	41 278	
<del>16</del>		J-12	4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	1 559	2.03	228	354 762	
47	1	-	4 bed DC/DA	+ TGS Peracidox	99.60	99.94	2 209	4.90	389	858 349	

Table 2: cost and operational data of techniques used to control SO<sub>2</sub> emissions in sulphuric acid production.

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4	1 <del>8</del>			4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	4 591	10.19	389	1 783 465	
				4 bed DC/DA	Base Case C2	99.60	-	0	0	0	0	914
4	<del>19</del>			4 bed DC/DA	+ Cs in bed 4	99.60	99.70	356	0.23	228	81 023	
	2 <del>0</del>	1000	9 - 12	4 bed DC/DA	5 bed DC/DA + Cs in bed 5	99.60	99.80	1 020	1.33	455	464 258	
4	24			4 bed DC/DA	+ TGS Peracidox	99.60	99.94	1 359	3.02	777	1 055 922	
	22			4 bed DC/DA	+ TGS (alkaline)	99.60	99.94	3 432	7.62	777	2 667 020	

#### Hypothesis:

- the conversion rate depends on specifications (design, installations, concentration, source of SO<sub>2</sub>). Precision 0,1%.
- SO<sub>2</sub> content: 5 7%: calculated with 5% and 9 12% calculated with 10%,
- $O_2$  content: 5 7%  $SO_2$  + 6 9%  $O_2$  and 9 12%  $SO_2$  + 8 11%  $O_2$ ,
- lifetime for all installations: 10 years,
- fixed operation costs: 3%,
- interest rate: 4%,
- price H<sub>2</sub>SO<sub>4</sub>: 20 €/t ex works
- labour costs: 37 k€/man-year
- utilities for TGS Peracidox and alkaline Absorptions: +30% capital investment costs
- warranted SO<sub>2</sub>-content after TGS: < 200 mg SO<sub>2</sub>/Nm<sup>3</sup> = < 70 ppm SO<sub>2</sub>
- steam price: 10 €/t
- SC = single contact ,SA = single absorption, DC = double contact, DA = double absorption

# 7.17.6 References used in chapter 7.17

- [1] Reference document on Best Available Techniques for the manufactures of large volume chemicals ammonia, acids and fertilizers, August 2007.
- [2] Comments from Birgit Brahner, German Federal Environment Agency, 12/2008.
- [3] "Compilation of the answers-to-questions-and proposal of EGTEI secretariat.doc",EGTEI, 02/2009.
- [4] Comments from Erik Kiekens, PVS, European sulphuric acid association, March 2009.
- [5] Comments from Dawn Christensen, Ineos, European sulphuric acid association, March 2009.
- [6] Comments from Aldo Zucca, Portovesme, European sulphuric acid association, March 2009.
- [7] Comments from Thomas Krutzler, UBA Austria, March 2009.
- [8] Retrofitting of old plants, ESA expert group, May 2009.

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# 7.18 Municipal, medical and hazardous waste incineration

#### 7.18.1 Coverage

This section addresses the incineration of municipal (or domestic) solid waste, hazardous and medical wastes as well as the incineration of sludges from wastewater treatment.

Municipal solid waste (MSW) mainly consists of paper and paperboard, glass, metals, plastics, rubber, leather, textiles, wood, food waste, yard waste, and miscellaneous inorganic waste [1].

Hazardous waste is mainly generated in industrial production processes (e.g. ashes, sludges, and other production waste), energy generation, civil engineering and building activities (e.g. demolition waste, construction site waste, and road construction waste) and by waste incineration (fly ashes) [1].

#### 7.18.2 Emission sources

Municipal solid waste, sewage sludge and hazardous waste can i. a. be treated in incineration plants. Municipal solid waste is mainly incinerated in public owned waste incineration plants, although a certain amount is burned at industrial incineration sites [1]

Different types of thermal treatments are applied to the different types of wastes, however not all thermal treatments are suited to all wastes. This paragraph describes the main technologies for the thermal treatment of wastes [1].

**Municipal solid waste** can be incinerated via several main combustion systems including moving grate and fluidized bed [1]. Fluidized bed technology requires MSW to be of a certain particle size range - this usually requires some degree of pre-treatment and/or the selective collection of the waste [3].

For the incineration of hazardous and medical waste, rotary kilns and grate incinerators are most commonly used, but fluidized bed incinerators are also applied.

**Incineration of sewage sludge** takes place in rotary kilns, multiple hearth, or fluidized bed incinerators, but co-combustion in grate firing systems, coal combustion plants and industrial processes is also applied [1], [2], [3]. Sewage sludge has to be dried or mechanically dehydrated before combustion and often additional firing is required to ensure stable combustion.

**Grate technology**. Municipal waste is the main application for these incinerators, which can be designed to handle large volumes of waste [2]. In Europe approximately 90% of installations treating MSW uses grates.

Different grate firing systems such as rocking grates, reciprocating grates, travelling grates, roller grates (each of them and water cooled or not) have been developed and can be distinguished by the way the waste is conveyed through the different zones in the combustion chamber. The different grate systems have to fulfill special requirements regarding primary air feeding, conveying velocity and raking, as well as mixing of the waste. Main additional features are good control characteristics and a robust construction to withstand the severe conditions in the combustion chamber [1].

**Fluidized bed Incinerators** are suitable only for reasonably homogeneous materials and are therefore the main designs for the incineration of sewage sludge, but also for mechanically or mechanically-biologically pre-treated waste streams [2].

Preheated air is introduced into the combustion chamber via openings in the bed plate forming a fluidized bed with the sand contained in the combustion chamber. The waste is fed to the reactor via a pump, a star feeder or a screw-tube conveyor. In the fluidized bed, drying, volatilisation, ignition, and combustion take place at a temperature between 850 and 950 °C. Above the fluidized bed, a secondary combustion zone is created to ensure a retention time of more than two seconds at a temperature above 850 °C. When the air supply to the fluidized bed is under-stoichiometrical (lambda

<1), the bed temperature is significantly lower, e.g. 650°C. In this case, only gasification takes place in the bed itself, and most of the heat is being generated in the secondary combustion zone, i.e. above the fluidized bed, by gas phase oxidation reactions [1].

Fluidized bed incineration systems have the advantage of easy and quick stop of waste supply and hot start behaviour and the advantage of a lower temperature which leads to lower NO<sub>x</sub> formation [1], [2]. However, in case of a complete shut-down (e.g. with the aim of bed material removal or maintenance work to be done) or a cold start, it takes significantly longer for a fluidized bed system to cool down or to heat up than for a grate system, as the whole sand load has to be cooled down or heated up to operation temperature

**Rotary kiln.** In rotary kilns, almost any waste, regardless of type and composition, can be incinerated and temperature restrictions for operation are not as stringent as in the case of fluidized bed or multiple hearth incinerators [1]. They have the benefit of good waste agitation and achieve good burnout, provided waste residence time in the furnace is adequate. They can be used in combination with other designs to provide additional ash burnout [2]. The rotary kiln consists of a cylindrical vessel slightly inclined on its horizontal axis. The waste is conveyed through the kiln by gravity as it rotates. In order to ensure complete destruction of toxic compounds, a secondary combustion chamber is generally necessary [Erreur ! Signet non défini.4].

**Multiple hearth furnaces** are mainly applied to the incineration of suldges. Sewage sludge is fed at the top of the furnace and moves downwards through the different hearths counter-current to the combustion air, which is fed at the bottom of the furnace. The upper hearths of the furnace provide a drying zone, where the sludge gives up moisture while the hot flue gases are cooled. The central hearths are in charge of the incineration, and the lower hearths ensure complete burnout. The incineration temperature is limited to 980 °C, because above this temperature the sludge ash fusion temperature will be reached and clinker will be formed. In order to prevent leakage of hot toxic flue gases, multiple hearth furnaces are always operated at a slight vacuum pressure [8]

**Other processes** have been developed that are based on the decoupling of the phases which also take place in an incinerator: drying, volatilisation, pyrolysis, carbonisation and oxidation of the waste; gasification using gasifying agents such as steam, air, carbon-oxides or oxygen is also applied.

#### 7.18.3 BAT, Associated Emission Levels (AEL)

#### 7.18.3.1 SO<sub>2</sub>

Sulphur dioxide as well as HCL and HF is formed during combustion of sulphur-(chloride- and fluoride)-containing compounds which are found in waste. Their amount is mainly determined by the amount of sulphur-(chloride- and fluoride) containing compounds present in the waste but operation conditions and incineration technology applied may also have a minor impact.

Raw gas concentrations of  $SO_2$  typically are in a range from 400 to 1000 mg/Nm<sup>3</sup>, clean gas concentrations are mostly required to be considerably lower [1], [3], making flue gas treatment indispensable.

 ${\rm SO}_2$  is removed in general from the flue gas by means of wet scrubbers, spray-dry scrubbers and dry scrubbers.

The use of primary measures such as fuel selection, waste selection or segregation techniques, are considered to be BAT [2].

The three main techniques, web scrubbing, semi-dry and dry scrubbing are considered to be BAT for the removal of  $SO_2$  in the incineration of sewage sludges, municipal and medical waste [2].

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For wet scrubbers and <u>semi-wet FGTsemi-dry scrubbers</u>, <u>concentration</u> < 20 mg/m<sup>3</sup> can be achieved and water consumption is needed (and effluent may be generated). Reduction rates of 96-98.4 % are achievable. For dry scrubbers, <u>concentration achieved can be</u> < 40-20 or to < 420 mg/m<sup>3</sup> <del>can be</del> achieved depending on the reagent used.

Table 1: Emission sources and selected BAT SOx control measures with associated emission levels in waste incineration

Emission source	Combination of control measures	Operational SOx emission level associated with BAT <sup>1 2</sup> (mg/Nm <sup>3</sup> )						
Do	mestic or municipal waste incine	ration						
Grate incinerator	Dry scrubber	1- 40 <del>[3]</del> [3]						
Rotary kiln	Spray dry scrubber	1 - 40						
Fluidized bed combustion	Wet Scrubber	1 - 40						
Industrial w	aste incineration (hazardous and	medical waste)						
Grate incinerator	Dry scrubber	1 - 40						
Rotary kiln	Spray dry scrubber	1 - 40						
Fluidized bed combustion	Wet Scrubber	1 - 40						
Inciner	ation of sludges from waste-wate	r treatment						
Rotary kiln	Dry scrubber	1 - 40						
Multiple hearth furnace	Spray dry scrubber	1 - 40						
Fluidized bed combustion	Wet Scrubber	1 - 40						
<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.								

<sup>2</sup> The ELV of the EU waste incineration directive for SO<sub>2</sub> is 50 mg/m<sup>3</sup>

#### 7.18.3.2 NOx

Nitrogen oxides are emitted from incineration plants. In many cases they are measured using continuous emission monitors. Emissions at modern plants are reported to be generally in the range between 30 and 200 mg/Nm<sup>3</sup>. (clean gas, daily average, 11%  $O_2$  [3]).

Emissions of NO<sub>x</sub> can generally be lowered by reducing the amount of incinerated waste. This can be accomplished through various waste management strategies, including recycling programmes and composting of organic materials.

Nitrogen oxides are formed predominantly as NO and NO<sub>2</sub>.-Contrary to high temperature processes, mest-<u>Most</u> of the nitrogen oxides generated during waste incineration (furnace temperature between 800 and 1200 °C) originate from the nitrogen contained in the waste (fuel-\_NO<sub>x</sub>) [1]. Thermal NO<sub>x</sub> concentrations are lower than fuel NO<sub>x</sub> concentrations. Therefore, the reduction efficiency of primary measures mainly aimed at limiting fuel NO<sub>x</sub> formation is generally limited, as a majority of nitrogen oxides (to a limited extent through changes in plant design and operation [1]. However, primary measures are generally of great importance for reducing the formation of NO<sub>x</sub> at the combustion stage. They mainly relate to the management and preparation of wastes, and particularly to the thermal treatment applied [3].

Primary measures (limiting emissions at the source in opposition to secondary measures reducing end of pipe emissions) have been developed to reduce  $NO_x$  emissions at source during the combustion process by regulating flame characteristics such as temperature and fuel-air mixing. Secondary measures operate downstream of the combustion process and remove  $NO_x$  emissions from the flue gas.

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For the incineration of sewage sludges as well as municipal and medical waste the use of primary measures such as flue-gas recirculation, air-staged combustion, fuel selection, low NOx burners in combination with secondary measures (e.g., SCR, SNCR) is considered to be BAT.

In general SCR is considered BAT where higher NO<sub>x</sub> reduction efficiencies are required (i.e. raw flue gas NO<sub>x</sub> levels are high) and where low final flue-gas emission concentrations of NO<sub>x</sub> are desired. Actually, SCR is a proven technology in the waste incineration sector, which allow to achieve high NO<sub>x</sub> reduction rates (typically over 90%)  $\frac{11-3}{11-3}$  and NO<sub>x</sub> emission of below 50 mg/m<sup>3</sup> [11].

For SNCR ammonia and urea injection are suitable and considered to be BAT. Reducing NO<sub>x</sub> by SNCR to 75% requires a higher addition of the reducing agent. With application of SNCR NO<sub>x</sub> emission concentrations of 70 mg/m<sup>3</sup> (daily average) [1], [3] can be reached.

An effective emission control of NOx via SCR or SNCR can result in increased  $NH_3$ -emissions ( $NH_3$ -slip), which again can be converted to  $NO_x$ . To achieve a low level of total nitrogen emissions also a  $NH_3$ -emission control ( $NH_3$  emissions < 10 mg/m<sup>3</sup> are achievable) is necessary [3].

Table 2: Emission sources and selected BAT NOx control measures with associated emission levels in waste incineration

Emission source	Combination of control measures	Operational NO <sub>x</sub> emission level associated with BAT <sup>1 2</sup> (mg/Nm <sup>3</sup> )
Waste incineration	SCR	40-100
	no SCR	120-180

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

 $^2$  The ELV of the EU waste incineration directive for NO\_x is 200-400 mg/m³ (depending on plant capacity and existing/new status)

Effective control of NOx abatement systems, including reagent dosing contributes to reducing NH3 emissions. Wet scrubbers absorb NH<sub>3</sub> and transfer it to the wastewater stream. BAT are considered NH3 emissions <10 mg/m<sup>3</sup> (BREF Split view: <5)

#### 7.18.3.3 Dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC)

Dust emissions from waste incineration plants mainly consist of the fine ashes from the incineration process that are entrained in the gas flow [3],[3].—Dust is normally measured continuously with reported emissions after treatment of between <0.05 and 15 mg/Nm<sup>3</sup> (11% O<sub>2</sub>) [3]).

Dust removal techniques can be divided into pre-dedusting and end-dedusting. Whereas the main purpose of pre-dedusting is to collect residues of different composition separately and to avoid operational problems in down-stream equipment, the main purpose of end-dedusting is to reduce final dust emissions

Dry and wet electrostatic precipitator and fabric filters are the mainly used three types for removing of particulate matter in flue gases. ESPs are effective in collecting dust with particle size in the range of 0.1 µm to 10 µm, and their overall collection efficiency can be 95 to 99 percent [1].

Fabric filters (FF) are considered to be BAT for the incineration of sewage sludge as well as municipal and medical waste. They are a proven technology and when correctly operated and maintained provide reliable abatement of particulate matter to below 5 mg/m<sup>3</sup>. Removal efficiencies are very high for a large range of particle size.

In general, electrostatic precipitators (ESPs) either wet or dry are not capable of abating particulate matter to the same extent as fabric filters [2]. In combination with wet scrubbers they are considered to be BAT. Depending on the design system and the place in the flue gas treatment system (pre- or end-dedusting), particulate emission concentration values of 5 to 25 mg/m<sup>3</sup> can be reached [Erreur !

Signet non défini.3]. With a wet ESP which is a specific version of the ESP the cleaning takes place continuously by a water flow. This version is applied as end-dedusting after a wet scrubber. Very low particulate matter of below 5 mg/m<sup>3</sup> can be reached [3].

Waste incineration is not identified as a large emitter of BC according to references [12], [13] and [14]. However BC emission data are scarce. If BC is present in dust, BAT measures described just above efficient for fine particles, are also efficient for BC.

 Table 3: Emission sources and selected BAT dust control measures with associated emission levels in waste incineration

	Emission source	Combination of control measures	Operational dust emission level associated with BAT <sup>1 2</sup> (mg/m <sup>3</sup> )	
Was	te incineration	FF, ESP In general the use of fabric filters gives, the lower levels within this emission range,	1-5	2

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded

<sup>2</sup> The ELV of the EU waste incineration directive for dust is 10 mg/m<sup>3</sup>

# 7.18.4 Cost data for emission reduction technologies

# Table 4: cost data for different abatement techniques [1], [3]

	Inves	tments costs (	EURO)	Specific costs of maintenance (EURO/t)				
Control options	Thro	ughput per lin	e (t/yr)	Throug	ghput per lin	e (t/yr)		
	75,000	100,000	150,000	75,000	100,000	150,000		
SCR	1,200,000	1,500,000	2,000,000	0.30	0.30	0.30		
SNCR	700,000	800,000	1,000,000	0.19	0.16	0.13		
Wet dedusting system	1,500,000	2,000,000	2,500,000	0.30	0.30	0.30		
Dry flue gas cleaning with adsorption	1,725,000	2,175,000	3,000,000	0.23	0.22	0.20		
ESP	1,000,000	1,200,00	1,600,000	0.27	0.24	0.21		
Dry flue gas cleaning with fabric filter	1,150,000	1,450,000	2,000,000	0.15	0.15	0.13		

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Guidance document on control techniques for emissions of sulphur, NOx, VOCs, dust and black carbonfrom stationary sources

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# 7.19 Industrial wood processing

# 7.19.1 Coverage

The wood processing industry is composed by many activities. Sawmill, flooring, panel production, furniture production are the main activities covered by this wide sector.

Wood processing is mainly a source of dust emissions.

This chapter covers the different activities of wood processing. Although, wood processing industries use wood to fed boilers, wood combustion is not included in this chapter.

# 7.19.2 Emission sources

Wood processing activities can be separated between primary and secondary processing steps. Primary processing covers raw wood processing activities while secondary processing covers activities transforming primary processed wood.

During primary processing, wood harvest is cut, barked, cross cut or pressed. Then, wood is secondary processed into wooden floor, panels, furniture, toys, etc.

Different types of wood are used in wood processing industry; they are presented in the following table. [1]

Table 1: wood processing activities (sources of dust emissions) associated to types of wood	
used	

Process	Dry wood	Moist wood	Timber	Panel
Wood harvest cut		Х	Х	
Slicing		Х	Х	
Primary cut		Х	Х	
Storage of fine sawdust and chips	Х	Х		
Defibration, milling and chipping		Х	Х	Х
Drying of laminations, particles and sawdust		Х	Х	Х
Screening				
Seasoning of timber and drying of panels			Х	Х
Pressing of panels	Х			Х
Cutting	Х		Х	Х
Sanding	Х		Х	Х
Other machining (edging, planning, etc.)	Х		Х	Х
Workshop cleaning	Х	Х	Х	Х

Dust emission levels and characteristics depend on 2 main factors:

- type of wood processed,
- water content of the wood processed.

Therefore, dry wood, moist wood, timber and panel are separated in the previous table.

# 7.19.3 Available Techniques, Associated Emission Level (AEL)

Techniques used to reduce dust emission levels depend on particle sizes, which themselves depend on the process applied and the wood used. Therefore, it is necessary to distinguish primary processing from secondary processing.

#### Primary processing steps [1]

Primary processing steps are essentially debarking, slicing, primary cutting, routing, milling, chipping and pressing. Those processes are not major sources of fine particle emissions. Emissions are mainly composed by particles with a diameter of more than 700 µm except from the routing process which is a source of particles with a diameter of more than 100 µm.

#### Debarking, slicing, primary cutting and routing:

During these processes, dust emissions are mainly coarse particles. To reduce dust emission levels, a spray of water on the trunk can be considered as sufficient during the debarking process which is a source of low emission levels while cyclones can be used to control dust emissions from slicing, primary cutting and routing which are sources of higher emission levels.

#### Milling and chipping:

In most of the cases, the mill grinder is open and dust emission levels are high. However emissions can be collected by an aspiration system and dust emission levels can be reduced by the use of fabric filters.

#### Pressing:

A wet electrostatic precipitator can be used to reduce dust emission levels from collected emissions of the pressing process.

#### Secondary processing steps [1]

Secondary wood processing steps are important issues concerning fine particle emissions. The higher level of  $PM_{10}$  and  $PM_{2,5}$  emissions can be explained by the fact that the wood used in secondary processing steps is dry.

Drying, sanding and edging processes are major sources of high dust emission levels. Mainly fine particles are emitted during these processes, thus emissions should be collected and treated. Multicyclones or a combination of cyclones and wet scrubbing system can be used to treat emissions from drying systems. Fabric filters can be used to reduce dust emission level from sanding or edging.

As heated air used in the dryers usually comes from boilers fed by wood fuel, dust come also from the boiler and emission levels need to be reduced before entering the dryer.

Collected dust from fabric filters or other dry dust reduction techniques should be recycled and re-used in the process as far as possible or used as biomass fuel. The collected dust or sawdust should be transported between the different process steps in closed conveyor equipped with an aspiration system and a dust treatment system.

Emissions from sawdust storages are mainly fugitives. Storages have thus to be protected from the wind and handled carefully. Good housekeeping may also contribute to reduce dust emissions.

Dust emissions can also be abated using electrostatic filters, but this technique is very expensive and does not seem to be cost effective in the wood processing industry. However it can be considered as available techniques for new installations while fabric filters can be considered as available techniques in existing installations for most emitting processing steps.

Panel production can be separated from other wood processing industries. In wood processing industries, small companies of less than 20 employees are numerous while panel production establishments are significantly larger in size. Therefore, secondary measures to reduce dust emission levels are more cost effective in panel industry than they are in other small wood processing industries.

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Table 2: associated dust emission levels with available techniques to reduce emissions in
panel production industry [1]

Emission source	Techniques	Associated emission level (mg/Nm³)
	Cyclone	100 – 230
Dryers in particle board	Wet scrubbing system	15 – 75
production	Combination of cyclone and wet scrubbing system	25
Dryers in fiberboard production	Cyclone	7
Machining in fiberboard production	Bag filters	0,03 - 0,6
Dryers in oriented strand board	Cyclone filter	60 – 70

# 7.19.4 Emerging techniques

No emerging technique is considered for the wood processing industry.

# 7.19.5 Cost data for emission reduction techniques

The following table gives an overview of the costs for different abatement techniques in particle board industry.

### Table 3: cost of techniques to control PM emission in particle board industry [2]

Technique	Investment ( Euros/1000m <sup>2</sup> of board) <sup>1</sup>
Cyclone	5.4
Wet Cyclone	7.2
Fabric Filters	21.6
Dry ESP	28.8
Wet ESP	32.3

<sup>1</sup>Conversion rate used: 1 C\$/1000m<sup>2</sup> = 7.19 €/1000m<sup>2</sup>.

# 7.19.6 References used in chapter 7.19

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# 7.20 Petrol distribution (from the mineral oil refinery dispatch station (petrol) to service stations including transport and depots (petrol))

# 7.20.1 Coverage

Activities covered relate to the transport and distribution of petrol from mineral oil refinery dispatch stations or terminals, to service-stations often via intermediate storages. The terminal is any facility which is used for the storage and loading of petrol onto road tankers, rail tankers, or vessels, including all storage installations on the site of the facility. A refinery may have its own terminal fed by pipeline in close proximity but external to the refinery site or a dispatch station which is located on the refinery. The service-station is an installation where petrol is dispensed to motor vehicle fuel tanks from stationary underground storage tanks [1].

# 7.20.2 Emission sources

At terminals, petrol is stored in External Floating Roof Tank (EFRT) or in Internal Floating Roof Tanks (IFRT).

Petrol transport is carried out by a combination of road, rail and water transport and by pipeline; this last means releases no significant emissions.

At terminals, different means are used for loading of mobile containers (road tankers, rail tankers, barges and marine tankers). Bottom loading and top loading of containers are used. VOC emissions depend on the type of container being loaded, the degree of saturation of the vapour in the cargo tank [2] and also how loading is carried out.

Petrol is delivered to service-stations where it is transferred into underground storage tanks and subsequently dispensed into automobile fuel tanks. At service-stations, filling of underground tanks is carried out via a fixed vertical pipe installed within the tank to which the road tanker is connected using a hose. VOC emissions occur from the storage tank loading and breathing although the latter is minimal as the tank is underground and hence not subject to diurnal changes in solar heating.

At service-stations, in addition to the emissions arising from fuel deliveries, there are emissions released from the refuelling of vehicles.

Vehicle-refuelling operations are considered to be a major source of VOC emissions. These emissions are attributable to vapour displaced from the automobile tank by dispensed petrol. The major factors affecting the quantity of emissions are the volume of petrol dispensed, petrol temperature, vehicle tank temperature, petrol vapour pressure, and dispensing rates. Especially, the vehicle tank temperature is nowadays of major importance for refuelling emissions of modern gasoline injection cars. These VOC emissions can be controlled by vapour balancing systems, so-called Stage II controls which have been legislated for on a national basis in a large number of EU countries or by an enlarged carbon canister system which is mandated in the USA.

# 7.20.3 BAT, Associated Emission Levels (AEL)

Emission control options from mobile tank filling and service-station storage tank filling are generally named stage I controls. In the EU, these activities are regulated under the European Parliament and Council Directive 94/63/EC of 20 December 1994 on the control of volatile organic compound emissions resulting from the storage of petrol and its distribution from terminals to service stations [1].

Emission control options concerning car refuelling are generally termed stage II controls.

In the scope of air thematic strategy programme, the EU has issued a proposal of directive related to stage II of petrol vapour recovery during refuelling of passenger cars [11]. BAT, associated emission levels.

### 7.20.3.1 Petrol storage

BAT are described in chapter 7.5.

#### 7.20.3.2 Stage I controls

Stage I controls mainly consist of vapour balance lines and vapour recovery units (VRU) to recover petrol. Modified loading, e.g. bottom loading of road tankers, results in a smaller vapour loss than top loading. Bottom loading enables reduced VOC emissions compared to top loading and importantly permits more efficient vapour collection than with modified top loading arms.

Vapours collected at service stations from the discharge of petrol from road tankers can be returned via the road tankers and recovered in the terminal VRU. The VRU unit is based on adsorption on activated carbon, absorption, membrane separation or hybrid systems combining cooling/absorption and compression/absorption/membrane separation [9]. The overall efficiency of VRU ranges from 95 to more than 99 % [9]. Stage I controls also mean modifications to road and rail tankers and to ships and barges. In the latter cases, extra care must be taken to maintain safety standards particularly to prevent propagation of ignition and over- or under-pressurisation of cargo tanks.

#### 7.20.3.3 Stage II controls

VOC emissions from car refuelling can be controlled by vapour balancing systems, so-called stage II controls, or by an enlargement of the on-board canister already installed on automobiles to capture fuel system hot soak losses. Stage II controls are technically capable of achieving a 85-92% recovery (depending on the capture efficiency). The costs of stage II are rather site-specific and vary widely.

To reduce VOC emissions from vehicle tank filling at service stations, active vapour recovery systems can be used. They are based on the following principle: the petrol air vapour mixture escaping from the tank during filling is sucked off at the vapour spout of the nozzle and vapours are returned back to the storage tank. The air/vapour mixture has to be returned proportionally to the flow rate of petrol delivered. Components of an open active petrol vapour recovery system include:

- a vapour recovery nozzle,
- a hose through which vapours are collected and a pipe through which the vapours are returned to the underground tank
- a vacuum pump and a system to control the ratio of the volume of vapour recovered to the volume of petrol dispensed in the vehicle tank.

The ratio Vapour/Petrol (V/P) has to range from 95 % to 105/110 % vol. Greater V/P ratio cannot be used to avoid excessive pressure built up and consequent VOC release through the pressure relief valves of the storage tank.

The control of the ratio can be achieved by a proportional valve controlled either hydraulically or electronically. Electronic regulation systems are the most widely used. However two systems can be distinguished: the Electronic Controlled Vapour Recovery (ECVR) – open loop – without regulation and the Electronic Controlled Vapour Recovery – Self Calibrating Gas – with regulation.

With active systems ECVR without regulation, VOC recovery efficiency cannot be maintained effectively during the entire life time of the system. If maintenance and checks are not operated carefully and periodically, efficiency decreases as the V/P ratio rapidly deviates from the optimal values. A leak on the vapour line will reduce the volume of vapour returned and hence the recovery efficiency.

With active systems ECVR with regulation, the control of vapour recovery is adjusted after each filling operation. Each deviation from the optimum value is compensated electronically. The efficiency is consequently stable during the life time of the system.

In both cases, theoretical VOC emission recovery efficiency is about 85 to 92 % wt. However in real life, the efficiency of the ECVR with regulation is constant and consequently larger than the efficiency of the ECVR without regulation. Faults can be detected and alarms can be installed to prevent operations outside optimal values. If a fault is detected, the petrol delivery can be de-activated until the fault is rectified [3]. This type of demand is presently implemented in some countries such as Germany, Switzerland and UK.

Although experience with the first generation of Stage II systems was poor, the combination of routine dry-tests (which electronically simulate the liquid flow and measure the air sucked in), regular visual

inspection by the service station personnel and the installation of a 'fault code' system (which check that the equipment is working properly e.g. that the vapour pump is functional and that the vapour control valves are operating within defined limits) can achieve consistently high recovery efficiencies at approximately one tenth of the cost of the automatic monitoring system.

To achieve an overall VOC recovery efficiency of about 95 % wt, the V/P ratio has to be increased by a factor 1.3 to 1.5 [4]. However, vapour recovery systems with V/P ratio larger than 100-110 % can only be used if additional types of systems able to prevent any excessive pressure and consequent VOC release through the pressure relief valves of the storage tank, are used. These systems are based on membranes or compression and condensation [4], [6]. As example, the membrane unit is installed in parallel to the vent stack of the petrol underground tank. The vapour sucked during car refuelling is always returned to the storage by an active system. However the V/P ratio used is higher. Consequently the surplus of vapours generates an over pressure in the storage tank. The pressure gauge of the vacuum pump of the membrane unit controls the pressure. At a certain pressure, the vacuum pump is activated and the tank pressure relieves over the membrane module to the atmosphere. A global efficiency of 95% is obtained according to reference 4.

Other vapour recovery systems can be used, in which petrol vapours are recovered at the dispenser and returned directly for sale. The equipment includes an active system to suck vapours with the vacuum pump, a heat exchanger and a compressor which condenses the petrol vapours and a tank in which water is separated from recovered petrol. The petrol recovered is conducted to the dispenser for refilling a vehicle.

Table 1:	associated	emission	levels	with	BAT	to redu	ce VOC	emissions	in	refinery	petrol
dispatch	station										

Emission source	BAT and reduction efficiency	BAT associated emission levels* kg VOC/m <sup>3</sup> /kPa [2], [9]
Road tanker filling, bottom or top loading and vapour balancing during previous off loading and VRU		0.0228 x 0.05 to 0.0228 x 0.01
Rail tanker, top loading and VRU	VRU with 95 to 99 % efficiency [9]	0.0108 x 0.05 to 0.0108 x 0.01
Marine tanker, typical cargo tank condition		0.004 x 0.05 to 0.004 x 0.01
Barge – typical cargo tank conditions		0.007x 0.05 to 0.007 x 0.01

\*Not available in reference [9] but calculated with reference [2].

# Table 2: associated emission levels with BAT to reduce VOC emissions in intermediate petrol storages

Intermediate depot			
Emission source	BAT and reduction efficiency	BAT associated emission level kg VOC /m <sup>3</sup> /kPa* [2], [9]	
Petrol storage	Internal floating roof External floating roof Other tank designs and appropriate colours 97 to 99.5 % compared to a fixed roof tank without measure [12]	Refer to the efficiency provided	
Road tanker filling, bottom or top loading and vapour balancing during previous off loading and VRU	VRU with 95 to 99 % efficiency [9]	0.0228 x 0.01 to 0.0228 x 0.05	

\*Not available in reference [9] but calculated with reference [2].

# Table 3: emission levels of available techniques to reduce VOC emissions from service-stations

	Service-stations		
VOC source	Available techniques	Reduction efficiency	Emission level kg VOC /m <sup>3</sup> /kPa [2] and [6]
Underground storage tank filling	Vapour return to the mobile container (breathing losses not covered)	Vapour return efficiency > 95 %	0.0011
Car refuelling	Well controlled and maintained active systems with common vapour/petrol ratio of 95 to 105 % v/v	Vapour recovery efficiency > 85% w/w	0.0367 x 0.15

kPa is the true vapour pressure of the product delivered, m<sup>3</sup> of petrol

# 7.20.4 Cost data for emission reduction techniques

Costs of stage I and stage II options are available for service-stations. Costs for service-stations depend on the size of the station. Costs can be estimated as presented in the following table. Investment costs for stage I come from the EGTEI data [5]. Investment costs for conventional ECVR without regulation at the dispenser come from manufacturer data [7] and costs of works from reference [8]. These costs have been determined for an ADEME study not yet published, made in 2007 by CITEPA [6].

#### Table 4: costs for stage I and stage II in service-stations of different sizes

		Emissions	Avoided emissions	Invest- ment	Operatio- nal cost	Total annual cost (10 years and 4 %	Cost per ton of VOC abated
		kg VOC/y	kg VOC/y	€	€/an	interest rate)€/an	€/t VOC avoided
510.4	No reduction	90					
RI01 < 100 m <sup>3</sup> / an	Stage I	59	32	6 400		789	24 955
	Stage I and II	16	74	14 300	100	1 863	25 194
	No reduction	588					
RI02 100 to 500 m <sup>3</sup> / an	Stage I	382	206	9 800		1 208	5 879
	Stage I and II	107	481	22 600	200	2 986	6 213
	No reduction	1 582	0				
RI03 500 to 1000 m <sup>3</sup> / an	Stage I	1 028	553	12 600		1 553	2 807
	Stage I and II	288	1 294	30 200	400	4 123	3 186
	No reduction	4 067					
RI04 1000 to 2000 m <sup>3</sup> / an	Stage I	2 645	1 423	15 200		1 874	1 317
1000 10 2000 111 / 411	Stage I and II	740	3 328	37 900	600	5 273	1 584
	No reduction	5 197					
RI05 2000 to 3000 m³/an	Stage I	3 379	1 818	17 500		2 158	1 187
2000 10 3000 11 /all	Stage I and II	945	4 252	45 000	800	6 348	1 493
	No reduction	7 909					
RI06 3000 to 4500 m <sup>3</sup> / an	Stage I	5 142	2 767	19 800		2 441	882
5500 to 4500 m / dl	Stage I and II	1 438	6 471	52 100	1 000	7 423	1 147
	No reduction	19 208					
RI07 > 4500 m <sup>3</sup> / an	Stage I	12 488	6 719	27 000		3 329	495
> 4000 III / all	Stage I and II	3 493	15 714	79 000	2 000	11 740	747

For active systems, the cost efficiency ratio depends on the size of stations and decreases with the decrease of the size. Costs range from 900 to  $1350 \notin / t$  VOC abated for stations larger than  $3000 \text{ m}^3$  per year,  $1700 - 1800 \notin / t$  VOC abated for stations from  $1000 \text{ to } 3000 \text{ m}^3$  per year and become larger for smaller stations :  $3500 \notin / t$  VOC abated for stations from  $500 \text{ to } 1000 \text{ m}^3$  per year,  $6500 \notin / t$  VOC abated for stations from  $25400 \notin / t$  VOC abated for stations delivering less than  $100 \text{ m}^3$  per year.

# 7.20.5 References used for chapter 7.20

[1] European Parliament and Council Directive 94/63/EC of 20 December 1994 on the control of volatile organic compound (NMVOC) emissions resulting from the storage of petrol and its distribution from terminals to service stations

[2] CONCAWE

Air pollutant emission estimation methods for E-PRTR reporting by refineries

Report n°1/2009 - 2009 edition

[3] VDI 4205 Part 5

Measurement and test methods for the assessment of vapour recovery systems on filling station

System test of automatic monitoring systems of active vapour recovery systems - September 2006 [4] Klaus Ohlrogge and Jim Wind

Membrane based vapour recovery at petrol stations - GKSS forchungszentrum

[5] EGTEI - Distribution of gasoline – Service stations - 2003

http://www.citepa.org/forums/egtei/egtei\_doc-Fuel\_distribution.htm

[6] NMVOC emissions from service stations – ADEME 2007- Not publicly available

VOC emissions from service stations - Synthesis - ADEME 2007 -

[7] TOKHEIM data provided to CITEPA – July 2006

[8] Data from Total - 2007

[9] European Commission - Reference document on best available techniques for mineral oil and gas refineries - BREF – February 2003 – European commission – Available at: <u>http://eipccb.jrc.es</u>

[10] EPA - Emission factor documentation for AP42 section 7.1 - Organic liquid storage tanks

Final report - September 2006

[11] Proposal for a European Parliament and Council Directive on Stage II petrol vapour recovery during refueling of passenger cars at service stations, {SEC(2008) 2937}, {SEC(2008) 2938} 4.12.2008, COM(2008) 812 final

[12] European Commission - reference document on BAT on emissions from storage – February 2003 – Available at: <u>http://eipccb.irc.es</u>

# 7.21 Storage and handling of organic compounds (except petrol covered by chapters 7.5 and 7.20)

## 7.21.1 Coverage

This chapter addresses the storage and handling of organic compound (vapour pressure higher than 10 Pa at 20°C) carried in activities such as the organic chemical industry, use of solvents, fine chemical industry, etc. Petrol storage and handling is covered by chapters 7.5 and 7.20.

### 7.21.2 Emission sources

Storage and handling of liquid organic compounds (vapour pressure higher than 10 Pa at 20°C) may be source of VOC emissions.

# 7.21.3 BAT, Associated Emission Levels (AELs)

BAT description comes from reference 1 and 2.

#### Storage

#### Tank design

BAT for a proper design is to take into account at least as follows:

- the physico-chemical properties of the substance being stored
- how the storage is operated, what level of instrumentation is needed, how many operators are required, and what their workload will be
- how the operators are informed of deviations from normal process conditions (alarms)
- how the storage is protected against deviations from normal process conditions (safety instructions, interlock systems, pressure relief devices, leak detection and containment, etc.)
- what equipment has to be installed, largely taking account of past experiences of the product (construction materials, valve quality, etc.)
- which maintenance and inspection plan needs to be implemented and how to ease the maintenance and inspection work (access, layout, etc.)
- how to deal with emergency situations (distances to other tanks, facilities and to the boundary, fire protection, access for emergency services such as the fire brigade, etc.).

#### Inspection and maintenance

BAT is to apply a tool to determine proactive maintenance plans and to develop risk-based inspection plans such as the risk and reliability based maintenance approach. Inspection work can be divided into routine inspections, in-service external inspections and outof-service internal inspections.

#### Tank colour

BAT is to apply either a tank colour with a reflectivity of thermal or light radiation of at least 70 %, or a solar shield on aboveground tanks which contain volatile substances.

# Emissions minimization principle in tank storage

BAT is to abate emissions from tank storage, transfer and handling.

#### External floating roof tank

The BAT associated emission reduction level for a large tank is at least 97 % (compared to a fixed roof tank without measures), which can be achieved when over at least 95 % of the circumference the gap between the roof and the wall is less than 3.2 mm and the seals are liquid mounted, mechanical

shoe seals. By installing liquid mounted primary seals and rim mounted secondary seals, a reduction in air emissions of up to 99.5 % (compared to a fixed roof tank without measures) can be achieved. However, the choice of seal is related to reliability, e.g. shoe seals are preferred for longevity and, therefore, for high turnovers.

BAT is to apply direct contact floating roofs (double-deck), however, existing non-contact floating roofs (pontoon) are also BAT.

Additional measures to reduce emissions are:

- applying a float in the slotted guide pole
- applying a sleeve over the slotted guide pole, and/or
- applying 'socks' over the roof legs.

#### Fixed roof tanks

Fixed roof tanks are used for the storage of flammable and other liquids, such as oil products and chemicals with all levels of toxicity.

For the storage of volatile substances which are toxic (T), very toxic (T+), or carcinogenic, mutagenic and reproductive toxic (CMR) categories 1 and 2 in a fixed roof tank, BAT is to apply a vapour treatment installation.

For other substances, BAT is to apply a vapour treatment installation, or to install an internal floating roof.

The selection of the vapour treatment technology is based on criteria such as cost, toxicity of the product, abatement efficiency, quantities of rest-emissions and possibilities for product or energy recovery, and has to be decided case-by-case. The BAT associated emission reduction is at least 98 % (compared to a fixed roof tank without measures).

The achievable emission reduction for a large tank using an internal floating roof is at least 97 % (compared to a fixed roof tank without measures), which can be achieved when over at least 95 % of the circumference of the gap between the roof and wall is less than 3.2 mm and the seals are liquid mounted, mechanical shoe seals. By applying liquid mounted primary seals and rim mounted secondary seals, even higher emission reductions can be achieved. However, the smaller the tank and the smaller the number of turnovers, the less effective the floating roof is.

#### Transfer and handling

#### Inspection and maintenance

BAT is to apply a tool to determine proactive maintenance plans and to develop risk-based inspection plans such as, the risk and reliability based maintenance approach;

#### Leak detection and repair programme

For large storage facilities, according to the properties of the products stored, BAT is to apply a leak detection and repair programme. Focus needs to be on those situations most likely to cause emissions (such as gas/light liquid, under high pressure and/or temperature duties).

#### Emissions minimisation principle in tank storage

BAT is to abate emissions from tank storage, transfer and handling that have a significant negative environmental effect, This is applicable to large storage facilities, allowing a certain time frame for implementation.

#### **Operational procedures and training**

BAT is to implement and follow adequate organisational measures and to enable the training and instruction of employees for safe and responsible operation of the installation

#### Piping

BAT is to apply aboveground closed piping in new situations. For existing underground piping it is BAT to apply a risk and reliability based maintenance approach.

Bolted flanges and gasket-sealed joints are an important source of fugitive emissions. BAT is to minimise the number of flanges by replacing them with welded connections, within the limitation of operational requirements for equipment maintenance or transfer system flexibility,

BAT for bolted flange connections include:

- fitting blind flanges to infrequently used fittings to prevent accidental opening
- using end caps or plugs on open-ended lines and not valves
- ensuring gaskets are selected appropriate to the process application
- ensuring the gasket is installed correctly
- ensuring the flange joint is assembled and loaded correctly
- where toxic, carcinogenic or other hazardous substances are transferred, fitting high integrity gaskets, such as spiral wound, kammprofile or ring joints.

Internal corrosion may be caused by the corrosive nature of the product being transferred, BAT is to prevent corrosion by:

- selecting construction material that is resistant to the product
- applying proper construction methods
- applying preventive maintenance, and
- where applicable, applying an internal coating or adding corrosion inhibitors.

To prevent the piping from external corrosion, BAT is to apply a one, two, or three layer coating system depending on the site-specific conditions (e.g. close to sea). Coating is normally not applied to plastic or stainless steel pipelines.

#### Vapour treatment

BAT is to apply vapour balancing or treatment on significant emissions from the loading and unloading of volatile substances to (or from) trucks, barges and ships. The significance of the emission depends on the substance and the volume that is emitted, and has to be decided on a case-by-case basis.

### Valves

BAT for valves include:

- correct selection of the packing material and construction for the process application
- with monitoring, focus on those valves most at risk (such as rising stem control valves in continual operation)
- applying rotating control valves or variable speed pumps instead of rising stem control valves
- where toxic, carcinogenic or other hazardous substances are involved, fit diaphragm, bellows, or double walled valves
- route relief valves back into the transfer or storage system or to a vapour treatment system.

#### Pumps and compressors

#### Installation and maintenance of pumps and compressors

The design, installation and operation of the pump or compressor heavily influence the life potential and reliability of the sealing system. The following are some of the main factors which constitute BAT:

- proper fixing of the pump or compressor unit to its base-plate or frame
- having connecting pipe forces within producers' recommendations
- proper design of suction pipework to minimise hydraulic imbalance
- alignment of shaft and casing within producers' recommendations
- alignment of driver/pump or compressor coupling within producers' recommendations when fitted
- correct level of balance of rotating parts
- effective priming of pumps and compressors prior to start-up operation of the pump and compressor within producers' recommended performance range (The optimum performance is achieved at its best efficiency point.)
- the level of net positive suction head available should always be in excess of the pump or compressor
- regular monitoring and maintenance of both rotating equipment and seal systems, combined with a repair or replacement programme.

#### Sealing system in pumps

BAT is to use the correct selection of pump and seal types for the process application, preferably pumps that are technologically designed to be tight such as canned motor pumps, magnetically coupled pumps, pumps with multiple mechanical seals and a quench or buffer system, pumps with multiple mechanical seals and seals dry to the atmosphere, diaphragm pumps or bellow pumps.

#### Sealing systems in compressors

BAT for compressors transferring non-toxic gases is to apply gas lubricated mechanical seals. BAT for compressors, transferring toxic gases is to apply double seals with a liquid or gas barrier and to purge the process side of the containment seal with an inert buffer gas. In very high pressure services, BAT is to apply a triple tandem seal system.

#### Table 1: associated Emission Levels with BAT to reduce VOC emissions from storage of organic compounds

Emission sources	Combination of BAT	BAT Associated Emissions Levels for VOCs
Storage tanks of volatile products	Internal floating roof External floating roof Other tank designs and appropriate colours	97 to 99.5 % compared to a fixed roof tank without measure*

\* If the efficiency cannot be reached because of the specific characteristics of a storage tank (such as small throughput, small diameter), best available primary and secondary seals have to used.

# 7.21.4 Cost data for emissions reduction techniques

.No cost data are available.

# 7.21.5 References used for chapter 7.21

[1] European Commission - reference document on BAT in emissions from storage - July 2006.

[2] European Commission - reference document on BAT on emissions from storage – February 2003 – Available at: <a href="http://eipccb.jrc.es">http://eipccb.jrc.es</a>

# 7.22 Manufacture of organic chemicals (Except production of organic fine chemicals, chapter 7.23)

# 7.22.1 Coverage

In this chapter, the organic chemical industry is the industry aiming at producing the following types of products :

- lower olefins such as ethylene and propylene produced mainly by the steam cracking route,
- aromatics compounds such as benzene and toluene,
- oxygenated compounds,
- nitrogened compounds,
- halogenated compounds,
- polymers (polyethylene, polypropylene, PVC, polyesters, polystyrene...).

# 7.22.2 Emission sources

In the production of organic chemicals, emissions differ widely according to the products and production processes. Often one product is produced by different processes, each of which has its own emission characteristics with regard to VOCs.

VOCs emissions arise from some main sources, as follows:

- fugitive emissions. Fugitive VOC emissions are released from leaking pressurised equipment components on process units, such as valves, flanges and connectors, opened lines and sampling systems containing volatile liquids or gases. Volatile products are defined in CEN 15446 [7] and reference [8] as all products of which at least 20% by weight has a vapour pressure higher than 0,3 kPa at 20°C,
- stack emissions,
- flaring systems (used for safe disposal of hydrocarbons or hydrogen that cannot be recovered in the process),
- storage and handling of chemical substances treated in chapter 7.21.

# 7.22.3 BAT, Associated Emission Levels (AEL)

### New installations:

When new processes are designed and in case of major modification of existing processes, BAT is a selection of the following techniques:

- carry out chemical reactions and separation processes continuously, in closed equipment,
- subject continuous purge streams from process vessels to the hierarchy of: re-use, recovery, combustion in air pollution control equipment and combustion in non dedicated equipment
- minimise energy use and maximise energy recovery,
- use compounds with low or lower vapour pressure.

Process modification, including changes of feedstock and products, can in selected cases help to reduce VOC emissions. New chemical reactions or principles may be applied to reduce the quantity of undesired by-products. Process improvements must also aim at recovery and recycling of by-products as well as at enclosing open process equipment as far as possible.

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An efficient measure to reduce waste gas flow rates and VOC emissions from oxidation and oxychlorination processes (e.g. production of vinyl chloride) is the use of pure oxygen instead of air. New oxidation and oxychlorination plant usually uses only pure oxygen.

#### Fugitive VOC emissions:

For preventing and controlling fugitive VOC emissions, BATs are a combination of leak detection and repair programme <u>ae-and</u>the use high performance equipment:

<u>Aa</u> leak detection and repair programme (LDAR) <u>consisting consists</u> in measuring the concentration of VOC in the atmosphere around the potential leak, then selecting equipments leaking over a defined threshold value and finally operating a repair on those leaking items.

A LDAR programme is established according to the following principles [6]:

- the definition of what constitutes a leak and fixation of corresponding thresholds,
- the fixation of the frequency of inspections,
- the listing and identification of components included,
- the procedures concerning repair of leaking components depending of the leak category.

Immediate minors repair can be carried out immediately such as tightening leaking equipment. Maintenance and complex repair have to be scheduled. They can be done during scheduled shutdown.

Equipment tightening can be made with equipment in operation (except with remote control valves (eg tightening bolts to eliminate leaks from valves stems or flanges, installing tightening caps on open ends----)-\_etc).

Maintenance with dismantling equipment or exchange, can only be carried out during plant shutdowns with circuit insulation and degassing. So, during plant shutdowns, two kinds of maintenance programme can be carried out according to the situation [6]:

- basic maintenance: maintenance on the equipment (flanges + valves) to remove some parts or to change the equipment with a new one of the same technology.
- heavy maintenance: complete change of the valves with valves of the higher grade standard, not leaking technology. Basic maintenance is maintained for the flanges.

<u>use H</u>high-performance equipment such as consists of the following [1]:

- valves: low leak rate valves with double packing seals, bellow seals for high risk duty,
- pumps: double seals with liquid or gas barrier, or seal pumps,
- compressors and vacuum pumps: double seals with liquid or gas barrier, or seal less pumps, or simple seal technology with equivalent emission levels,
- flanges: minimise the number, use effective gaskets,
- open ends: fir blind flanges, caps and plugs to infrequently used fittings, use closed loop flush on liquid sampling points, and for sampling systems analysers optimise the sampling volume/frequency, minimise the length of sampling lines or fit enclosures,
- safety valves: fit upstream rupture disk.

#### Stack VOC emissions:

VOC in vent gases can be controlled by conventional methods of controlling organic pollutants from stationary sources, i.e. adsorption, absorption, condensation, membrane process, thermal and catalytic incineration, as well as process modification. These techniques are presented in chapter 5.3.2.

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#### Flare emissions:

- for preventing flare emissions, BAT is:
- minimise the need for hydrocarbon disposal to flare through good plant design and good plant management
- BAT for elevated flare design and operation includes the provision of permanent pilots and pilots flame detection, efficient mixing, ratio controlled to the hydrocarbon flow and remote monitoring by closed circuit television
- destruction efficiency larger than 99% for elevated flare and 99.5 % for ground flares.

### VOC from storage, handling and transfer [1] and [2]:

BAT for **storage, handling and transfer** is, in addition to those described in chapter 7.2221, an appropriate combination or selection of, *inter alia*, the following techniques:

- external floating roof with secondary seals (not for highly dangerous substances), fixed roof:
- tanks with internal floating covers and rim seals (for more volatile liquids), fixed roof tanks;
- with inert gas blanket, pressurised storage (for highly dangerous or odorous substances);
- inter-connect storage vessels and mobile containers with balance lines;
- minimise the storage temperature;
- instrumentation and procedures to prevent overfilling:
- impermeable secondary containment with a capacity of 110 % of the largest tank;
- recover VOCs from vents (by condensation, absorption or adsorption) before recycling or
  - destruction by combustion in an energy raising unit, incinerator or flare;
- continuous monitoring of liquid level and changes in liquid level;
- tank filling pipes that extend beneath the liquid surface;
- bottom loading to avoid splashing;
- sensing devices on loading arms to detect undue movement:
- self-sealing hose connections / dry break coupling.

## 7.22.4 Cost data for emission reduction techniques

Unit costs range from -100 to + 180 €/t VOC abated according to the reduction measure considered according to EGTEI [9] for implementing a LDAR programme to reduce fugitive emissions for the steam cracking unit. Negative costs indicate that savings are high and counter balance.

Unit costs range can be much larger and range as example from 310 to 1050 €/t VOC abated according to the reduction measure considered in the production of PVC [10].

# 7.22.5 References used for chapter 7.2322

[1] European Commission - Reference document on BAT in the large volume organic chemical industry – February 2003

[2] European Commission - Reference document on BAT in the production of polymers – 2006

[3] European Commission - Reference document on BAT for the manufacture of organic fine chemicals August 2006

[4] European Commission - reference document on BAT in common waste water and waste gas treatment / management systems in the chemical sector – February 2003.

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[5] European Commission - reference document on BAT in <u>on emissions from</u> storage to be completed February 2003July 2006.

[6] EGTEI background document on the organic chemical industry.

 [7] EN15446:2008 Fugitive and diffuse emissions of common concern to industry sectors -Measurement of fugitive emission of vapours generating from equipment and piping leaks
 [8] EPA - Protocol for equipment leak - Emission estimates EPA 453-95-017 – 1995

[9] EGTEI - Organic chemical industry - steam cracking - synopsis sheet - 15 October 2005

http://www.citepa.org/forums/egtei/10-Synopsis-sheet-steam-cracking-15-10-05.pdf

[10] EGTEI - Organic chemical industry - Production of PVC - synopsis sheet - 3 October 2005

http://www.citepa.org/forums/egtei/11-synopsis-sheet-PVC-suspension-03-10-05.pdf

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# 7.23 Production of organic fine chemicals

# 7.23.1 Coverage

The speciality organic chemical industry covers the production of different types of chemicals produced in campaign basis, in multi purpose and multi product plants (pharmaceutical active ingredients, biological products, food additives, photographic chemicals, dyestuffs and intermediates, pesticides and other speciality products...) [1].

The pharmaceutical product manufacturing is part of the organic chemical industry and covers both:

- the production of primary pharmaceutical products: production of bulk pharmaceuticals, drug intermediates and active ingredients by means of synthesis, fermentation, extraction or other processes, in multipurpose and multi product plants and on a campaign basis.
- the activities related to formulation of finished drugs and medicines using the active ingredients supplied by the bulk plants (taking place in finishing plants). Active ingredients are converted into products suitable for administration. Physical formulation, filling and packaging are involved.

Only VOC emissions are covered in this chapter.

# 7.23.2 Emission sources

This industry is very heterogeneous: plants manufacture a large range of products, using a large number of production processes and may store and use several hundred raw material substances or intermediate products. Processes are usually operated on a campaign basis and in multi purpose plants. For one active ingredient, several transformation stages are required. The processes typically involve between 1 to 40 transformation stages depending on molecules. Process stages cover the full range of unit operations such as: reactions, liquid/liquid extraction, liquid/liquid or liquid/solid or gas/solid separation, distillation, crystallisation, drying, gas adsorption...<u>etc.</u> Production is carried out in discontinuous processes (or batch processes). Equipment is rarely specific but, most often, multi application. Processes frequently use solvents. Any reacted raw materials may be either recovered or recycled or ultimately discharged to the environment after appropriate treatment.

Due to the diversity of processes used in this sector, no simple process description can be made. Instead, a brief outline of characteristics of existing pharmaceutical product production plants is provided.

#### Significant number of VOC emission release points

Gaseous discharge circuits are complex. For the same equipment, several discharge points often exist, depending on the performed operations. The large number of discharge points is due to:

- quality constraints required in this sector in order to avoid risks of cross-contamination,
- security constraints in order, for example, to avoid the contact of incompatible gases.

Plants having an annual solvent consumption ranging from 900 to 1 500 t may have from 10 to 50 VOC emission vent stacks in the atmosphere.

A large number of discharge points are equipped with condensers to trap VOCs. To trap corrosive or toxic gases, several vents are related to abatement absorption columns. When secondary abatement techniques are applied, collecting the vents proves to be necessary.

#### High variability of VOC discharges with time

VOC concentrations may vary widely from one discharge point to another. Discharges with high waste gas flow rates and low concentrations do exist; general ventilation of a factory belongs to this group. Other discharges, such as production equipment vents are characterised by very low waste gas flow rates (some  $Nm^3/h$ ) and VOC concentrations that may be high.

VOC discharges present a very high variability over time: high variability over time when there is a discharge and non-permanent discharges.

This situation leads to more significant costs for emission treatment: the gas-cleaning device should be able to accept emission peaks. Abatement technique dimensioning must be based on the peak discharge (the frequency of peaks should be considered as well). Investments are thus higher than for more regular emissions in time.

#### A large number of solvents used

In this activity, even though 5 solvents (methanol, toluene, acetone, ethanol, methane dichloride) represent about 70 % of the new solvent consumption [1], around 40 different solvents are in use. The consumption of chlorinated solvents is still quite high. This large number of solvents, the presence of chlorinated solvents and security and quality constraints make the use of secondary abatement techniques more difficult and more expensive (treatment of HCl if incineration, limited potential for collection and recycling of solvents).

# 7.23.3 BAT, Associated Emission Levels (AEL)

In order to reduce solvent losses and emissions into the atmosphere, a wide range of best practices and process improvements are available among which work in concentrated environment in order to reduce the consumption of solvents, increased use of low volatile solvents and of solvents easier to condense, modification of certain operating conditions for distillation (e. g. distillation under ordinary pressure instead of vacuum distillation), implementation of good housekeeping, increased condenser efficiency (increased exchanger surfaces and increased refrigerating capacities), technology change (dry-sealed vacuum pumps instead of liquid ring vacuum pumps; closed pressure filters or vacuum filters more leak free than open filters; vacuum dryers leading to a better solvent condensation....).

A list of BAT is a follows [2]:

- contain and enclose sources and close any openings in order to minimise uncontrolled emissions,
- carry out drying using closed circuits, including condensers for solvent recovery,
- keep equipment closed for rinsing and cleaning with solvents,
- close unnecessary openings in order to prevent air being sucked to the gas collection system via the process equipment,
- ensure the air tightness of process equipment, especially of vessels,
- apply shock inertisation instead of continuous inertisation,
- minimise the exhaust gas volume from distillations by optimisation of the layout of the condenser,
- carry out liquid addition into vessels as bottom feed or with dip leg, unless reaction chemistry and / or safety considerations make it impractical. In such cases, the addition of liquid as top feed with a pipe directed to the wall reduces splashing and hence the organic load of the displaced gas,
- minimise the accumulation of peak loads and flows and related concentration peaks by optimisation of the production matrix and application of smoothing filters.
- treatment of waste gases containing VOC. The selection of VOC treatment techniques is a crucial task on a multipurpose site. Since the volume flows show a wide variation on a multipurpose site, the key parameter for the selection of techniques are average mass flows from emission point sources in kg/hour. One or a combination of techniques can be applied as a recovery/abatement system for a whole site, an individual production building, or an individual process. This depends on the particular situation and affects the number of point sources. Nonoxidative recovery/abatement techniques are operated efficiently after minimisation of volume flows and the achieved concentration levels should be related to the corresponding volume flow

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without dilution by, e.g. volume flows from building or room ventilation. Thermal oxidation/incineration and catalytic oxidation are proven techniques for destroying VOCs with highest efficiency but show considerable cross-media effects. In direct comparison, Catalytic oxidation consumes less energy and creates less NOx and hence is preferred where technically possible. Thermal oxidation is advantageous where support fuel can be replaced by organic liquid waste (e.g. waste solvents which are technically/economically available on-site and non-recoverable) or where autothermal operation can be enabled by stripping of organic compounds from waste water streams. Where exhaust gases also contain high loads of other pollutants besides VOCs, thermal oxidation can enable, e.g. the recovery of marketable HCl or, if the thermal oxidiser is equipped with a DeNOx unit or is designed as two stage combustion, the efficient abatement of NOx.Thermal oxidation/incineration and catalytic oxidation can also be a suitable technique to reduce odour emissions.

#### BAT is to reduce emissions to the levels given

Existing installations can reduce their total VOC emissions to less than 5 % of the solvent input by following a combined strategy which involves:

a) Step-by-step implementation of integrated measures to prevent/reduce diffuse/fugitive emissions and to minimise the mass flow that requires abatement

b) Applying high level recovery/abatement techniques, such as thermal/catalytic oxidation or activated carbon adsorption

c) Applying specific recovery/abatement techniques at source on smaller sites with dedicated equipment, and by utilising only one or two different bulk solvents.

# Table 1: selected VOC control measures with BAT associated VOC emission levels for organic fine chemicals

Emission source	Combination of control measures	BAT associated emission levels for VOC
New plants	Mix of BAT defined above (primary measures and use of secondary measures (both oxidation, adsorption and / or condensation))	≤ 3 % of solvent input*
Existing plants	Mix of BAT defined above (primary measures and use of secondary measures (both oxidation, adsorption and / or condensation))	≤ 5% of solvent input*

\* Sum of 11 the quantity of organic solvents or their quantity in preparations purchased which are used as input into the process in the time frame over which the mass balance is being calculated + 12 the quantity of organic solvents or their quantity in preparations recovered and reused as solvent input into the process. (The recycled solvent is counted every time it is used to carry out the activity.)

# Table 2: BAT Associated VOC Emission Levels for non-oxidative recovery/abatement techniques [2]

Process step	Average emission level from point sources*		
Non-oxidative recovery/abatement techniques	0.1 kg C/hour* or 20 mg C/m3**		
*The averaging time relates to the emission profile, the levels relate to dry gas and Nm3 **The concentration level relates to volume flows without dilution by, e.g. volume flows from room or building ventilation			

# Table 3: BAT associated emission levels for total organic C for thermal oxidation/incineration or catalytic oxidation [2]

Process step	Average emission level from point sources*			
Thermal oxidation/incineration or catalytic oxidation	Average mass flow < 0.05 kg C/h**	or	Average concentration** < 5 mg C/m <sup>3</sup>	
* The averaging time relates to the emission profile, levels relate to dry gas and Nm <sup>3</sup> These values are technically demanding and attention has to be carried out on energy efficiency which might be not acceptable				

# 7.23.4 Cost data for emission reduction technique

Costs vary in a large range. Average investments to achieve best performance levels on an existing plant are about 6700 k€ and the total costs per kg of abated VOC of 2.3 €/kg [8].

# 7.23.5 Reference used for chapter 7.23

[1] Speciality organic chemical industry. EGTEI background document – 24 may 2005

http://www.citepa.org/forums/egtei/speciality\_chemistry\_290405.pdf

[2] European commission - reference document on BAT for the manufacture of organic fine chemicals August 2006

[3] Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31999L0013:EN:HTML

[4] Regulation (EC) No 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC

[5] Arrêté du 31 janvier 2008 relatif au registre et à la déclaration annuelle des émissions polluantes et des déchets - (JO n° 62 du 13 mars 2008)

[6] Comments from André Peeters Weem, Cees Braams from InfoMil, the Dutch Ministry of Environment on GD 7-26 Manufacture of organic fine chemical - version 1

[7] Comments from Johannes Drotleff, German Umweltbundesamt on GD 7-26 Manufacture of organic fine chemical - version 1

[8] Speciality organic chemical industry. Synopsis sheet – 3 October 2005

http://www.citepa.org/forums/egtei/31-Synopsis-sheet-Speciality-organic-chemical-industry-03-10-05.pdf

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# 7.24 Adhesive coating (including footwear manufacture)

### 7.24.1 Coverage

Sectors using adhesives are very diverse. Production processes and application techniques are also very different. Relevant sectors are: the production of adhesive tapes, composite foils, the transportation sector (passenger cars, commercial vehicles, mobile homes, rail vehicles, aircrafts), the manufacture of shoes and leather goods and the wood material and furniture industry. The non-industrial use of adhesives is a large sector but it is studied separately.

# 7.24.2 Emission sources

Application techniques and types of adhesives used differ widely from one sector to another. Adhesives can be applied manually, by spraying, or roller coating. The application efficiency depends on the type of technique used. Solvent contents in the adhesives depend highly on the type of material consumed. Solvent content in solvent-based adhesives can be as high as 80%. Dispersion glues contain some 2 - 6 % solvents; and melting glues are solvent-free. Each type of adhesive has different physical and chemical properties.

# 7.24.3 BAT, Associated Emission Levels (AEL)

BAT AEL and techniques are based on STS BREF [1] for the manufacture of adhesive tapes and on EGTEI data [2] for the other sectors.

Reduction techniques are general but are suitable among sectors using adhesives.

Solvent-based adhesive coating processes generate significant amounts of VOC emissions, which can be reduced either by primary measures (substitution by zero or low organic solvent containing adhesives) or by secondary measures for larger installations (adsorption, thermal or catalytic oxidation). A selection of such measures applied to selected base processes is given in table 1.

Table 1: Emission sources and selected VOC control measures with	associated emission
levels for adhesive coating and shoe manufacturing	

Type of installation	Combination of control measures	Associated emission levels for VOC [Defined for the following averaging period: (yearly average for total AEL])
Manufacturing of adhesive tape	Use of condensation, adsorption, oxidation or a combination of these techniques	Total emission of 5 wt-% or less of the solvent input [1]
Manufacturing of adhesive tape Adhesive coating in other sectors	Use of non-solvent based adhesives	0 g/kg adhesive [2]
	Use of condensation, adsorption, oxidation or a combination of these techniques	< 150 g/kg adhesive [5]
	Use of water-based adhesives	20 g/kg adhesive [2]
Shoe industry	Use of water-based adhesives	20 – 30 g / pair [3]
	Use of biofiltration	

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# 7.24.4 Cost data for emission reduction techniques

Costs vary between about 0.1 and 0.7 k $\in$ /t VOC abated according to the type of measure applied (i.e. treatment or solvent consumption reduction): abatement costs are even less expensive with 100% solid content adhesives compared to solvent-based products but these systems are not always technically applicable. These costs are representative for large installations.

For the particular sector of shoe manufacturing, the implementation of thermal oxidation will lead to abatement costs around 8 to 11 k $\in$ /t VOC and the use of water-based products around 0.7 k $\in$ /t VOC but this last technique does not seem to be applicable to all types of productions.

The detailed methodologies used to estimate these costs are defined in EGTEI documents concerning "adhesive application" [2] and "manufacture of shoes" [3].

Caution: these documents are susceptible to evolve if new updated data are available.

# 7.24.5 Emerging techniques

No data is available.

# 7.24.6 References used for chapter 7.24

[1] STS BREF - August 2007

[2] EGTEI background document/synopsis sheet: Adhesive application – 2003/2005

[3] EGTEI background document/synopsis sheet: Manufacture of shoes - 2003/2005

[4] Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[5] Comments from Birgit Mahrwald - UBA

7.25 Coating processes 1: coating of cars, truck cabins, trucks and buses

# 7.25.1 Coverage

This sector covers the coating of passenger cars, truck cabins, trucks and buses.

# 7.25.2 Emission sources

Major steps of such processes may include:

- preliminary cleaning, phosphating, electrophoretic coating (also called electrocoating or electrodeposition);
- application of primer, curing of primer;
- application of topcoat(s), curing of topcoat(s);
- under body sealing and sealing of seams, cavity corrosion protection, and repair painting before assembly.

# 7.25.3 BAT, Associated Emission Levels (AEL)

BAT AELs are based on STS BREF [1]. Combinations of control measures are derived from discussion with ACEA [2] and correspond to the BAT.

# Table 1: emission sources and selected VOC control measures with associated emission levels for coating processes

Type of installation	Combination of control measures [4]	BAT associated emission levels for VOC
		[Defined for the following averaging period:[-yearly average for total AEL]]
Manufacture of cars (M1, M2)	Electrocoat: water-based (5 wt% solvent content) Primer: water-based (8 wt% solvent content) - electrostatic application Topcoat : - High solid coat (45 wt% solvent content) - electrostatic application, <b>and</b> - water-based basecoat (15 wt % solvent content) – electrostatic application – and solvent-based clear coat (45 – 55 wt% solvent content) - electrostatic application Solvent management plan, recovery of purge solvent	10 – 35 g VOC/m² or 0.3 kg/body + 8 g/m² to 1 kg/body + 26 g/m²
Manufacture of truck cabins (N1, N2, N3)	WB enamels HS clearcoat Improved solvent recovery / solvent consumption reduction Oxidation on ovens	10 – 55 g VOC/m²

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Manufacture of trucks (N1, N2, N3)	WB primer and topcoat for high runners and HS topcoat for special orders Improved solvent recovery / solvent consumption reduction	15 – 50 g VOC/m²
Manufacture of buses (M3)	Cataphoresis WB enamels HS clearcoat Improved solvent recovery / solvent consumption reduction Oxidation on cataphoresis, mid- layer and enamel ovens	92 – 150 g VOC/m²
Manufacture of vans	WB enamels HS clearcoat Improved solvent recovery / solvent consumption reduction Oxidation on ovens	15 – 50 g VOC/m²

The surface area is defined as the total electrophoretic coating area, and the surface area of any parts that might be added in successive phases of the coating process which are coated with the same coatings as those used for the product in question, or the total surface of the total product coated in the installations.

M1: vehicles used for the carriage of passengers and comprising not more than eight seats in addition to the driver's seat.

M2: vehicles used for the carriage of passengers and comprising more than eight seats in addition to the driver's seat, and having a maximum mass not exceeding 5 Mg.

M3: vehicles used for the carriage of passengers and comprising more than eight seats in addition to the driver's seat, and having a maximum mass exceeding 5 Mg.

N1: vehicles used for the carriage of goods and having a maximum mass not exceeding 3.5 Mg.

N2: vehicles used for the carriage of goods and having a maximum mass exceeding 3.5 Mg but not exceeding 12 Mg.

N3: vehicles used for the carriage of goods and having a maximum mass exceeding 12 Mg.

# 7.25.4 Cost data for emission reduction techniques

Costs are defined in the EGTEI documents "car coating" [3], truck and van coating [4], truck cabin coating [5] and bus coating [6].

For the manufacture of cars, abatement costs corresponding to BAT vary from 11 to 25 k€/tonne of VOC abated. Some techniques have even higher costs.

For the manufacture of trucks and vans, abatement costs vary between 12 k€/t VOC and 22 k€/t VOC abated depending on the associated emission level reached (i.e. Solvent Directive requirements or BAT).

For the manufacture of trucks cabins, abatement costs vary between 21 k $\in$ /t VOC and 33 k $\in$ /t VOC abated depending on the associated emission level reached (i.e. Solvent Directive requirements or BAT).

For the manufacture of busses, abatement costs vary between 13 k€/t VOC and 23 k€/t VOC abated depending on the associated emission level reached (i.e. Solvent Directive requirements or BAT).

The detailed methodologies used to estimate these costs are defined in EGTEI documents concerning "car coating" [3], "truck coating" [4], "truck cabin coating" [5] and "bus coating" [6].

Caution: these documents are susceptible to evolve if new updated data are available.

# 7.25.5 Emerging techniques

No quantitative data is available.

# 7.25.6 References used for chapter 7.25

[1] STS BREF - August 2007

[2] Internal meeting ACEA / EGTEI - July 2006

[3] EGTEI background document/synopsis sheet: Car coating - 2003/2005

[4] EGTEI background document/synopsis sheet: Truck coating - 2003/2005

 $\label{eq:stars} \ensuremath{\left[5\right]}\xspace{-1.5} \ensuremath{\mathsf{EGTEI}}\xspace{-1.5} \ensuremath{\mathsf{background}}\xspace{-1.5} \ensuremath{\mathsf{commut}}\xspace{-1.5} \ensuremath{$ 

[6] EGTEI background document/synopsis sheet: Bus coating - 2003/2005

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# 7.26 Coating processes 2: Winding wire coating

## 7.26.1 Coverage

Only the coating of metallic conductors used for winding the coils in transformers, motors, etc. is considered in this section.

## 7.26.2 Emission sources

Wires are coated by passing continuously through a bath of enamel. Coated wires are then dried in a heated chamber where solvents are evaporated and the film is cured a-t <u>a-hirehigh</u> temperature. Up to 30 applications of enamel may be applied until the desired layer thickness is obtained. Recirculated airflow ovens are in use in contemporary wire coating processes. The air/solvent mix is usually treated in a catalytic oxidiser which ensures that residual solvent concentrations are below legal threshold limits (typically  $20 - 30 \text{ mg C/Nm}^3$ ). The heat from the thermal oxidiser can be used in the drying process [1].

Depending on the final product requirements, a film of wax may be applied to the surface of the enamelled wire before it is wound on to a delivery reel. Traditionally, typical paraffin is applied from an organic solvent with a solvent content from 98 to 99.9%. Lubricants, as concentrated emulsions, with a solvent content between 50 to 95%, water-based emulsions or even solvent-free hot melts are also used in this industry, though with limited success [1].

There are now two methods available for applying solid wax to the wire surface. One method uses wax coated string in contact with the surface and the other is by applying a molten wax to the surface of the wire.

## 7.26.3 BAT, Associated Emission Levels (AEL)

Abatement options based on the STS BREF [1] are defined in the table 1 bellow.

Table 1: emission sources and selected VOC control measures with associated emission levels for winding wire coating

Emission source	Combination of control measures	BAT associated emission levels for VOC <del>[Defined for the</del> following averaging period: (yearly <u>average</u> for total AEL <u>]</u> )
All plants	Use of low solvent-based materials (such as high solids enamel coatings and solvent-free lubricants) and/or processes And	5 g/kg wire or less for non-fine wires (> 0.1 mm diameter)
	Use of catalytic oxidiser to treat emissions from the enamel coating step	10 g/kg wire or less for fine wires (0.01 - 0.1 mm diameter)

## 7.26.4 Cost data for emission reduction techniques

Costs are defined in the EGTEI documents concerning "wire coating" [2]. Abatement costs (€/tonne of VOC abated) are considered to be negative as when an oven is replaced, the only choice is to buy a more efficient one leading to energy savings.

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# 7.26.5 Emerging techniques

Waxing of fine wires: this technique is considered the solvent emissions from the final drying of wax on fine wires (0.01 - 0.1 mm) [1].

# 7.26.6 References used for chapter 7.26

[1] STS BREF - August 2007

[2] EGTEI background document/synopsis sheet: Wire coating - 2003/2005

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# 7.27 Coating processes 3: Coil coating

## 7.27.1 Coverage

Coil coating (of metal coil surface) is a linear process by which protective and/or decorative organic coatings are applied to flat metal sheets or strips packaged in rolls or coils.

# 7.27.2 Emission sources

The metal strip is sent through a coating application station, where rollers coat one or both sides of the metal strip. Roller coaters assure a very high transfer efficiency of the paint on the strip. The strip then passes through an oven where the coatings are dried and cured. As the strip exits the oven, it is cooled by water spray and/or air quenching and again dried. If the line is a tandem line, as most are, there is first the application of a primer, followed by another of topcoat on one or both sides of the strip.

Solvent-based paints containing between 40 and 50% of solvent are commonly used. There is no technical limit for the use of solvent-based paints.

# 7.27.3 BAT, Associated Emissions Levels (AEL)

The potential of use of the different coatings is different. Water-based paints almost disappeared in the early 80s and have not seen significant usage since due to technical difficulties in manufacture and limitations in use. The use of powder coatings is limited as their application is still technologically and economically difficult. For the time being, powder line speed is about 10 m/min vs. 50 - 100 m/min for most liquid paint lines, while film thicknesses less than  $60\mu$ m are difficult and expensive to achieve in powder. These factors combined make powder uncompetitive against traditional solvent-based coil coatings in most applications.

BAT AELs are based on the STS BREF [1] and on information from ECCA [4]. They are presented in table 1 bellow.

Table 1: emission sources and selected VOC control measures with associated emission levels for coil coating

Emission source	Combination of control measures	BAT associated emission levels for VOC [Defined for the following averaging periods:[-daily average for AELc and yearly average for AELf and total AEL]
Coil coating – new plants	Combination of extraction of the coating preparation area, paint application, drier/oven and cooling zone and treatment of the waste gases by thermal or catalytic oxidation	0.73 to 0.84 g NMVOC/m <sup>2</sup> , with 3 – 5% fugitive emissions* (concentrations in the treated waste gas of 20 - 50 mg C/m <sup>3</sup> can be reached)
Coil coating – existing plants		0.73 to 0.84 g NMVOC/m <sup>2</sup> , with 3 – 10% fugitive emissions* (concentrations in the treated waste gas of 20 - 50 mg C/m <sup>3</sup> can be reached)

\* New information from ECCA shows that the achievable emission rate depends on a wide variety of factors, but that a figure of <2.5 g/m<sup>2</sup> should be used to cover all foreseeable scenarios, where BAT is adopted. As this value has not been validated in the BREF, it is not reproduced in the table above.

## 7.27.4 Cost data for emission reduction techniques

Abatement costs corresponding to the implementation of a thermal oxidiser vary between about 200 and 360  $\in$ /t VOC abated according to the size of the installation. The detailed methodology used to estimate these costs is defined in the EGTEI synopsis sheet concerning "coil coating" [2].

Caution: this document is susceptible to evolve if new updated data are available.

## 7.27.5 Emerging techniques

The primary technique is secondary abatement through oxidisers. Technology for water-borne and powder paints are not new, but both systems suffer severe limitations. In the future, the emergence of radiation-curable paints (using UV and/or EB radiation) may provide VOC-free paint systems for this sector, but these technologies are not yet commercially adopted [4].

## 7.27.6 References used for chapter 7.27

[1] STS BREF – August 2007

[2] EGTEI synopsis sheet: Coil coating – 2006

[3] Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[4] Comments from ECCA - 09/03/2009

# 7.28 Coating processes 4: coating of metal, wood, plastic and other surfaces (fabric, leather, paper...<u>etc</u>)

## 7.28.1 Coverage

Only industrial uses of paints are considered in this section. The use of domestic and architectural paints is studied in another paragraph. Coating of cars and other vehicles, coil coating and coating of winding wire are defined in other sections as abatement techniques applied are very specific.

## 7.28.2 Emission sources

Within this source category, VOC emissions are released from the application of paint, from drying ovens and from the cleaning of equipment and paint cabins. According to reference [1], due to the high variety of techniques used and the highly different requirements for the quality of coatings, uniform reduction techniques can not be defined.

The requirements of the surface coating show significant differences within the sectors of paint application. The solvent content of products is very variable:

#### a/ Solvent based paints

Conventional solvent based paints contain approximately 30 to 80 wt. % of organic solvents.

High solid paints have a solid content above 65%.

#### b/ Water based paints

Water based paints contain from less than 1% to 18% of organic solvents used as solubilizer and for the improvement of properties of the wet film layer.

These paints are available and are widely used. Their range of application is increasing continuously.

#### c/ Powder coatings

Powder coatings are solvent free materials. Most often, overspray is recycled so the transfer efficiency is pretty high. For drying, the material is heated and thus merged into a film. Powder coatings are mainly applied via electrostatic assisted spraying on the work pieces. In several sectors, this technique is well established.

#### 7.28.3 BAT, Associated Emissions Levels (AEL)

BAT AELs are based on the STS BREF [2] for large installations consuming more than 200 tones of solvent a year and on the SED Directive [3] for smaller installations (associated emission factors are based on solvent reduction scheme calculations).

#### a/ General issues

The typical exhaust air from the coating industry has a high flow rate and a low organic solvent content, which means that energy costs for end-of-pipe measures can be significant. Therefore, if this option is chosen, processes should be used that have low energy consumption and/or high energy recovery rates. A further solution is to use a preceding concentration step via adsorption/desorption processes. The use of low and no organic solvent paints and cleaning methods is in many cases the most effective means of reducing organic solvent emissions in industrial painting.

Furthermore, for industrial applications, emission reduction technologies exist, such as improvement of the application processes: e.g. electrostatic guns and other spray techniques instead of conventional pneumatic application, low solvent-based coating systems, and sometimes automatisation of application. Also, paint recovery (e.g. overspray recovery) is a proven VOC abatement option in the wood- and metal-coating sectors.

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# b/ Specific issues for the wood coating

In the coating of wood materials, water-based coatings are not suitable with oak; powder coatings are only suitable for MDF (Medium-density fiberboard) and radiation cured coatings are suitable for flat pieces only.

Table 1: emission sources and selected VOC control measures with associated emission levels
for coating processes

Type of installation Large installations [2]	Combination of control measures	BAT associated emission levels for VOC [Defined for the following averaging period:( yearly <u>average</u> for total AEL])
Coating of furniture and wood materials	Waste gas treatment such as thermal oxidation when other techniques are not available or do not achieve suitable levels	0.25 kg or less of VOC / kg of solid input
	Use of low or non-solvent paints and, maximize efficiency of paint application	
	High organic solvent paints (solvent content of w-% 65) with high application efficiency technique (rolling, flooding, electrostatically assisted spraying, airless spraying) and good housekeeping	40 – 60 g VOC/m²
	Medium organic solvent paints (solvent content of w-% 20) with high application efficiency technique and good housekeeping	10 – 20 g VOC/m²
	Low organic solvent paints (solvent content of w-% 5) with high application efficiency technique and good housekeeping	2 – 5 g VOC/m²
Coating of plastic workpieces	Waste gas treatment	0.25 to 0.35 kg or less of VOC /
	Use of low solvent paints or water-based paints and, maximize efficiency of paint application	kg of solid input
Coating of metal surfaces	Waste gas treatment	0.10 to 0.33 kg or less of VOC /
	Use of low solvent paints or water-based paints and, maximize efficiency of paint application	kg of solid input
Small installations [3]		
Coating of furniture and wood materials	Waste gas treatment such as thermal oxidation when other techniques are not available or do not achieve suitable levels	1 to 1.6 (for installation consuming less than 25 tonnes of solvents per year) or less of VOC / kg of solid input

	Use of low or non-solvent paints and, maximize efficiency of paint application	
	Use of low solvent paints or water-based paints and, maximize efficiency of paint application	
Coating of metal and plastic	Waste gas treatment	0.375 – 0.6 (for installation
surfaces	Use of low solvent paints or water-based paints and, maximize efficiency of paint application	consuming less than 15 tonnes of solvents per year) or less of VOC / kg of solid input

According to CEPE [7], for metal and plastic coating 0.375 kg VOC emission per kg NV consumption is achievable by a combination of very high solids primer and high solids topcoat wet-on-wet which is a suitable process for many applications. Lower limits may apply for metal surfaces in cases where electrocoat, powder or other high-bake materials can be used. It might be unachievable for many low bake operations and would trigger need for abatement of spray-booth exhaust air as undesired add-on measure.

#### 7.28.4 Costs

Costs are defined in the EGTEI documents concerning "paint in the general industry" [4] and "wood coating" [5].

For the coating in the industry (general industry, continuous processes, plastic coating), abatement costs vary between 2 and 18 k€/tonne of VOC abated depending on the size of the installation and are negative for primary measures (higher application process efficiencies lead to the reduction of solvent consumptions so less products are used).

For the coating of wood, abatement costs vary from 2 to 16 k€/tonne of VOC abated depending on the size of the installation and are negative if emissions are reduced by primary measures.

Caution: these documents are susceptible to evolve if new updated data are available.

## 7.28.5 Emerging techniques

The electrostatically assisted application of powder coatings onto non-conductive wood and wood materials is under development [2].

## 7.28.6 References used in chapter 7.28

[1] BAT for paint and adhesive applications in Germany, IFARE - 2002

[2] STS BREF - August 2007

[3] Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[4] EGTEI background document/synopsis sheet: Paint in the general industry – 2003/2005

[5] EGTEI background document/synopsis sheet: Wood coating - 2003/2005

[6] Compilation of the answers-to-questions-and proposal of EGTEI secretariat.doc - EGTEI - 02/2009

[7] Comments from CEPE - March 2009

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# 7.29 Solvent content in products 1: Decorative coatings

## 7.29.1 Coverage

Decorative paints are applied in situ to buildings.

## 7.29.2 Emission sources

VOC emissions from decorative paint use come from evaporation of VOCs, which may be present as necessary components of the supplied paint or added before application of solvent based paints to reduce viscosity (thinners) or used as cleaning solvents [3].

All unrecovered VOCs can be considered as potential emissions. The major factor affecting these emissions is the amount of VOC in the ready for use paint. Paints can be water based - where the viscosity can be reduced by addition of water - or solvent based where the viscosity is reduced by addition of solvent.

Conventional solvent based decorative paints typically contained around 50% solids and 50% organic solvent. The VOC limits of the Product Directive 2004/42/EC [1] require adoption of lower VOC products.

## 7.29.3 Available techniques, Achievable Solvent Concentrations

Decorative paint VOC emissions result from use of the ready for use paint and from cleaning of equipment where this is done with solvents. VOC emissions can be reduced by adoption of lower VOC paint e.g. by switching use of conventional solvent based paint to lower VOC water based paint or by adopting lower VOC solvent based paints. The maximum VOC contents permitted under the phase II of the Product Directive 2004/42/EC are defined by product category in table 1 below.

	,, , , , , , , , , , , , , , , , , , ,		
Product Subcategory	Туре	Phase II (g/I)*	
Interior matt wall and ceilings	WB	30	
(Gloss ≤ 25@60°)	SB	30	
Interior glossy walls and ceilings	WB	100	
(Gloss > 25@60°)	SB	100	
Exterior walls of mineral substrate	WB	40	
	SB	430	
Interior/exterior trim and cladding paints for	WB	130	
wood and metal	SB	300	
Interior/exterior trim varnishes and woodstains,	WB	130	
including opaque woodstains	SB	700	
Primers	WB	30	
Finiters	SB	350	
adiag avimana	WB	30	
Binding primers	SB	750	
Dne pack performance coatings	WB	140	
	SB	500	
2 pack reactive performance coatings for	WB	140	
specific end use	SB	500	
Multi-coloured coatings	WB	100	
un-coloureu coannys	SB	100	
Decorative offects coatings	WB	200	
Decorative effects coatings	SB	200	

#### Table 1: achievable solvent concentrations for each type of paint

g/l ready to use

With the exceptions of solvent based interior wall paints, the European Decorative paints industry believes that in practice these VOC's should be achievable.

Interior wall paints will become entirely water based as the 30g/l and 100g/l limits will not be practically achievable with solvent based products [3].

## 7.29.4 Cost data

Costs are defined in the EGTEI background document concerning "decorative paint" [2]. According to CEPE [3], this document is outdated. CEPE has prepared a document covering the costs of relabeling products: this document is available to the group [4].

# 7.29.5 Emerging techniques

No data is available.

#### 7.29.6 References used for chapter 7.29

[1] Directive 2004/42/EC of the European Parliament and of the Council of 21 April 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in decorative paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC

[2] EGTEI background document: Decorative paint - 2003

[3] J. WARNON – CEPE – 02/03/2009

[4] Cost impact of Directive 2004/42/EC. CEPE estimate of relabeling costs for the changes in 2010 for Decorative paints

# 7.30 Manufacturing of coatings, varnishes, inks and adhesives

#### 7.30.1 Coverage

This sector covers the manufacturing of all types of paints, varnishes, stains as well as inks and adhesives. A wide number of products, formulated to meet a variety of service requirements, are available. These products are destined among others to aircrafts, automobiles, ships, wooden and metal furniture, packaging, textile fibres, domestic uses etc.

#### 7.30.2 Emission sources

Raw materials used in the products manufacturing process include solids, binders, solvents and all kinds of additives.

- solids provide the coating with colour, opacity, and a degree of durability.
- binders are components which form a continuous phase, hold the solids in the dry film, and cause it to adhere to the surface to be coated. The majority of binders are composed of resins and drying oils which are to a great extent responsible for the protective and general mechanical properties of the film.
- for viscosity adjustment, solvents are required. Materials that can be used as solvents include aliphatic and aromatic hydrocarbons, alcohols, esters and ketones.
- additives are raw materials which are added in small concentrations. They perform a special function or give a certain property to the coating. Additives include driers, thickeners, antifoams, dispersing agents, and catalysts.

Only physical processes such as weighing, mixing, grinding, tinting, thinning, and packaging take place; no chemical reactions are involved. These processes are carried out in large mixing tanks at approximately room temperature.

Emission losses may arise from several steps in the process. Major emission sources are:

- losses during filling and cleaning activities;
- losses from product clinging to the vessels and equipment;
- fugitive losses during mixing of preparations and storage of solvents.

## 7.30.3 Available Techniques, Associated Emissions Levels (AEL)

In the production of coatings, process modifications are possible by switching to low organic solvent containing paints and glues. Process controls for reducing emissions, such as covering vessels or reducing storage tank breathing losses can be implemented. Further VOC abatement options are condensation, adsorption, thermal and catalytic oxidation. Examples of available emission reduction measures are given in table 1 below.

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# Table 1: emission sources and selected VOC control measures with associated emission levels for manufacturing of paints and adhesives

Emission source	Combination of control measures	Associated emission levels for VOC [Defined for the following averaging period:( yearly average for total AEL])
Large installations with an annual organic solvent consumption > 1000 t		1 wt-% of solvent input [1]
All other plants	Good practices such as: Recovery of solvent vapours during raw material distribution, Unloading of the barrels with fork lifts to avoid leakages, Coverage of mobile vessels, Use of solvents with lower volatility to reduce fugitive emissions, Use of cleaning agents containing less solvents, Use of automatic cleaning devices whenever possible, Recycling of cleaning solutions,	2.5 wt-% of solvent input
	Good practices and upgrading of the condensation or carbon adsorption units and solvent recovery	1.75 wt-% of solvent input

## 7.30.4 Cost data for emission reduction techniques

Abatement costs corresponding to emission levels below 2% of the solvent input are about 2,200 €/t VOC abated. The detailed methodology is defined in the EGTEI synopsis sheet concerning "manufacture of paints, inks and glues" [2].

Caution: this document is susceptible to evolve if new updated data are available.

# 7.30.5 Emerging techniques

No data available.

# 7.30.6 References used for chapter 7.30

[1] Comments from UBA - this correspond to the German legislation for large installations

[2] EGTEI synopsis sheet: Manufacture of paints, inks and glues - 2005

# 7.31 Printing processes

#### 7.31.1 Coverage

The most important techniques in the printing sector are heatset offset, flexography and rotogravure in the packaging sector, publication gravure and rotary screen printing.

According to Intergraf [10], sheetfed and coldset have very limited VOC emissions. These emissions are also difficult to measure since there is no forced drying process producing waste gasses. There is a trend towards the use of low volatility cleaning agents and the avoidance of isopropanol in dampening solutions. The applicability of these emission reduction measures however depends very much on locally determined circumstances and cannot be translated in any kind of emission limit value. For this reason, these processes cannot be covered in the system used for the other printing processes and should be left out of this document.

#### 7.31.2 Emission sources

#### a/ Heatset offset

Offset means a printing process using an image carrier in which the printing and non-printing areas are on the same plane. The non-printing area is treated to attract water and thus reject the greasy ink. The printing area is treated to receive and transmit ink to a rubber coated cylinder and from there the surface to be printed.

Heatset means an offset printing process where evaporation takes place in an oven where hot air is used to heat the printed material (most offset inks do not dry by evaporation, but by oxidation or absorption in the paper. Heat set inks are the exception. They are the only offset ink drying largely through evaporation [1]).

Emissions to air arise primarily from the organic solvents contained in inks. Inks used within consist of high boiling mineral oils as solvents (between 40 and 45 wt.-%). About 20% of the mineral oil remains in the paper, where once cooled to room temperature, no longer fall within the definition of NMVOC, and the rest evaporates during the drying stage, which occurs at high temperatures (200 to 300 °C).

Solvents used in cleaning, the storage and handling of solvents and the use of organic solvents as part of the dampening solutions (commonly isopropanol) are also important sources of emissions of organic compounds.

#### b/ Publication gravure

Rotogravure means a printing process using a cylindrical image carrier, in which the printing area is below the non-printing area, using liquid inks that dry through evaporation. The cells are filled with ink and the surplus is cleaned off the non-printing area before the surface to be printed contacts the cylinder and lifts the ink from the cells. Only toluene based inks are used [1]. Ink contains 50% of toluene when leaving the ink factory. A dilution is made in the printing plant to obtain the proper concentration in toluene: machine ready ink contains up to 80% toluene [2]. This dilution is made with toluene recovered inside the plant.

#### c/ Flexography and rotogravure in packaging

Flexography means a printing process using an image carrier of rubber or elastic photopolymers on which the printing areas are above the non-printing areas, using liquid inks that dry through the evaporation of organic solvents. The process is usually web fed and is employed for medium or long multicolour runs on a variety of substrates, including heavy paper, fibreboard, and metal and plastic foil. The major categories of the flexography market are flexible packaging and laminates, multiwall bags, milk cartons, gift wrap, folding cartons, corrugated paperboard (which is sheet fed), paper cups and plates, labels, tapes, and envelopes. Almost all milk cartons and multiwall bags and half of all flexible packaging are printed by this process.

Solvent based inks can have different solvent contents when bought but ready to use inks contain about 80 to 90% of solvents (these figures take into account cleaning agents). Substitution can be implemented with water-based products (containing about 5% of solvent), UV curing inks and 2-

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components adhesives. Water-based inks in flexography printing are in regular production use in some packaging applications such as paper bags and plastic carrier bags [1].

# 7.31.3 BAT, Associated Emissions Levels (AEL)

BAT AEL and techniques are based on the STS BREF [3] when information is available (for large installations consuming more than 200 tones of solvents a year) and on the SED Directive [4] or EGTEI data for smaller installations. For screen printing, data are based on a study from 1999 [5] as this sector has not been treated specifically by EGTEI.

#### a/ Heatset Offset

NMVOC emissions from *heatset printing* consist of isopropanol (IPA) emitted from the dampening solutions, from cleaning agents and the stack emissions from dryers. BAT is to reduce the sum of fugitive emissions and to treat stack VOC emissions with thermal, catalytic or regenerative oxidation.

It is then BAT to reduce:

- the emission of IPA by using low IPA or free-IP dampening solution,
- fugitive emissions from the cleaning process by a combination of the following techniques: substitution and control of NMVOC used in cleaning, automatic cleaning systems for printing and blanket cylinders.

Type of press	BAT associated emission levels for VOC [Defined for the following averaging periods:[-daily_average for AELc and yearly average for AELf and total AEL]	
IPPC installations [1]		
For new and upgraded presses 2.5 to 10% VOC expressed as % of the ink consumpti weight		
For existing presses	5 to 15% VOC expressed as % of the ink consumption by weight	
Smaller installations		
For all presses	Fugitive emissions lower than 30% of solvent input can be reached [1] with concentration in the stack not greater than 20 mg C / $Nm^3$	

#### Table 1: BAT associated emission levels for heatset offset

#### **b/ Publication gravure**

In the *publication rotogravure* sector, more than 90% of the organic solvent consumption can be recovered, if activated carbon adsorption is used, due to the small number of components in the organic solvent (mainly toluene). The recycling of these organic solvents is possible and has long been practiced.

It is BAT to reduce fugitive emissions remaining after gas treatment:

#### Table 2: BAT associated emission levels for publication rotogravure

	For new installations [3]
	[Defined for the following averaging periods:( yearly average for total AEL])
	Total emissions of 4 to 5% of solvent input
	For existing installations [3], [4]
Ì	[Defined for the following averaging periods:( yearly average for total AEL])
	Total emissions of 5 to 7% of solvent input

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#### c/ Packaging rotogravure and flexography

In the *packaging rotogravure and flexography* sector, the following control measures for VOC emissions can be used:

Substitution with low solvent or solvent-free inks, and adhesives where practicable;

Activated carbon adsorption: the efficiency of the capturing system is an important parameter for the overall efficiency. Due to the numerous organic solvents in the inks, recycling on-site is difficult. This option may be technically and economically feasible for large printing installations with an annual solvent consumption of at least 500 Mg. The optimisation of the captured air flow at the different parts of an installation is always advisable when designing an installation. Minimizing the overall air flow rate and thus increasing the inlet concentration results in considerable savings in investments and operating costs;

Thermal or catalytic oxidation: the efficiency of the capturing system is an important parameter for the overall efficiency. At present, this measure is the most commonly used to reduce VOC emissions in this part of the printing sector, and it is expected to remain the most favourable option from an economic point of view for printing facilities with a solvent consumption of less than 500 Mg/year. The optimization of the captured air flow at the different parts of an installation is always advisable when designing an installation. Minimizing the overall air flow rate and thus increasing the inlet concentration results in considerable savings in investments and operating costs.

Table 3: emission sources and selected VOC control measures with associated emission levels
for packaging rotogravure and flexography

Type of installation	Combination of control measures	BAT associated emission levels for VOC [Defined for the following averaging periods:( daily average for AELc and yearly average for AELf and total AEL]
IPPC installations	For plants with all machines connected to oxidation For plants with all machines connected to carbon adsorption	7.5 to 12.5% of the reference emission <sup><math>\frac{2}{1}</math></sup> [3] 10 to 15% of the reference emission <sup><math>\frac{2}{1}</math></sup> [3]
	For existing mixed plants: where some existing machines may not be attached to an incinerator or solvent recovery	Emissions from the machines connected to oxidisers or carbon adsorption are below the emission limits of 7.5 to 12.5% or 10 to 15% respectively For machines not connected to gas treatment: use of low solvent or solvent free products, connection to waste gas treatment when there is spare capacity and preferentially run high solvent content work on machines connected to waste gas treatment. Total emissions below 25% of reference emission (requirement reduction scheme SED)
Smaller installations	AELc = 100 mg C/Nm <sup>3</sup> and AELf = 20 wt-% Or total AEL = 25% of reference emission <sup><math>\#</math></sup> which can be reached with the following measures	
	Switch to water-based inks (5 wt% solvent content)	50 g/kg of product ready to use (Abatement efficiency ~ 94%) [6]

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Guidance document on control techniques for emissions of sulphur, NOx, VOCs and dust (including PM10, PM	12,5
and black carbon), from stationary sources	

Solvent based products and treatment of stack emissions by oxidation	
60% of products with no-solvents and treatment of stack emissions for the remaining 40%	~ 80 g/kg of product ready to use (Abatement efficiency ~ 90%) [6]

a/Using the reference emission defined in annex IIb to the SED [4]

#### 7.31.4 Cost data for emission reduction techniques

The detailed methodologies developed to estimate costs are defined in the EGTEI synopsis sheets concerning "heatset offset" [6], "packaging" [7], and "publication gravure" [8].

Caution: these documents are susceptible to evolve if new updated data are available.

For *heatset offset*, abatement costs for the implementation of an oxidiser vary between about 1 and 5  $k \in$  according to the size of installations.

For the *packaging industry*, abatement costs are very dependant of the installation's size: for small installations, the use of an oxidiser costs around 22 k $\in$ /t NMVOC abated versus less than 1 k $\in$ /t NMVOC for the biggest installations. For all types of installations, <u>when the use of water-based inks is technically feasible</u>, this option will lead to costs around 0.15 k $\in$ /t NMVOC abated. The last option, technically and economically available only for large installations, is the implementation of carbon adsorption leading to abatement costs below 1 k $\in$ /t NMVOC.

For the *publication gravure*, abatement costs to reduce emissions by carbon adsorption are about 1 k€. Abatement costs are reduced because a large amount of toluene can be recycled.

#### 7.31.5 Emerging techniques

It is likely that UV curing flexo printing, for purposes other than beverage cartons, will be developed in the future [3].

### 7.31.6 References used for chapter 7.31

[1] P. VERSPOOR for INTERGRAF – Communications for EGTEI and IIASA – 2002 to 2004

[2] J. BERNARD for ERA. - 2003

[3] STS BREF – August 2007

[4] Directive 1999/13/EC of 11 March 1999. on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[5] Task Force on the Assessment of Abatement Options/Techniques for VOC from Stationary Sources – 1999

[6] EGTEI synopsis sheets: Heatset offset - 2005

[7] EGTEI synopsis sheets: Packaging - 2005

[8] EGTEI synopsis sheets: Publication gravure – 2005

[9] Compilation of the answers-to-questions-and proposal of EGTEI secretariat.doc - EGTEI - 02/2009

[10] Comments from Intergraf - 25/03/2009 and 25/05/2009

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# 7.32 Rubber processing

## 7.32.1 Coverage

This sector concerns the production of tyres as well as the production of all other rubber goods. Adhesives used in the production of some rubber goods are considered in the section on adhesive coating. Reduction techniques are not the same as the one defined below.

## 7.32.2 Emission sources

Products made of rubber are produced using a large variety of materials. The main process steps are:

- mixing;
- extrusion;
- calendering;
- building;
- curing (Vulcanisation).

Within the conversion of natural or synthetic rubber, organic solvents are mainly used for tackifying.

## 7.32.3 Available techniques, Associated Emissions Levels (AEL)

Reference documents on Best Available Techniques in the production of tyre and general rubber goods do not exist. The existing document addresses "Production of Polymers" which is not covered by the sector named "rubber processing" [4].

In this sector, VOC emissions will be reduced either by primary or secondary measures but generally, not by a combination of the 2 approaches. Most of the time, emissions will be reduced by switching solvent-based to low or non-solvent based products. When no technique is available, waste gas treatment might be used. Associated emission factors are based on the EGTEI document for the production of tyres [1] and on a study from 1999 for the production of rubber goods [2]. Considering the very large variety of installations and products manufactured and the fact that no BREF has been developed for this sector, achievable emission levels defined in table 1 are only **indicative** and have to be understood as average values.

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# Table 1: emission sources and selected VOC control measures with associated emission levels for the production of natural or synthetic rubber goods

Emission source	Combination of control measures	VOC emission levels [Defined for the following averaging period:( yearly average for total AEL)]	
Rubber goods production			
Plant with a solvent consumption ≥ 15 tonnes /year	Partly switch from solvent-based to water- based agents and cleaning systems or	1 kg/tonne rubber produced [2]	
	waste gas treatment such as oxidation		
Tyre production			
All plants	New processes (example: adhesive rubber band use – New type of building machine associated with extruder – New technology extrusion). Use of 25 % solvent-based adhesives, coatings, inks and cleaning agents (90 wt % solvent content)	2.5 kg/t of tyre [1] <sup>(1)</sup>	
	or oxidation when reduction of solvent consumption is not suitable		

(1) The VOC emission level of 2.5 kg VOC/t of tyre is derived from the EGTEI background document on tyre production [1]. This is the result of the application of a 75% reduction to the average non-abated situation (which includes also plants in which reduction measures had been already implemented)

# 7.32.4 Cost data for emission reduction techniques

Costs are defined in the EGTEI synopsis sheet concerning "tyre production" [1].

For the production of tyres, abatement costs defined, for an average installation, vary between 0.14 and 1 k€/tonne of VOC abated according to the technique implemented (i.e. solvent consumption reduction or thermal oxidation). In most of the cases, secondary measures will be implemented only when primary measures are not technically applicable.

Caution: this document is susceptible to evolve if new updated data are available.

## 7.32.5 Emerging techniques

No data is available.

## 7.32.6 References used for chapter 7.32

[1] EGTEI synopsis sheet: Tyre production – 2005

[2] Task Force on the Assessment of Abatement Options/Techniques for VOC from Stationary Sources – 1999

[3] Comments from ETRMA – March/April 2009

# 7.33 Dry cleaning

## 7.33.1 Coverage

This sector covers dry cleaning of textiles, leather and furs. Dry cleaning relates to cleaning of fabrics with organic solvents.

## 7.33.2 Emission sources

In dry-cleaning, solvents such as perchloroethylene (PER) and light hydrocarbons (which are flammable) are mainly used today. Hydrocarbons with higher flash point are also used. In Germany where these solvents are used in dry cleaning, the requirements for use are as follows [6]: ebullition temperature between 180 and 210 °C, flash point larger than 55°C. They are less volatile than perchlorethylene. Consequently the drying cycle is longer. They have a lower Kb value than PER and are consequently less efficient than PER for some types of products to be removed (the Kauri butanol value (Kb) measures the cleaning power of the solvent, the higher the Kb, the more aggressive is the solvent).

Significant VOC emissions of solvents from dry-cleaning machines can be divided into two categories:

- discharge of vapour, including venting of machines, air discharge from storage tanks during filling, leaks and solvent retained temporarily on cleaned clothes;
- residues left outside.

Presently some other types of organic solvent emerge. One of them is the Siloxane D<sub>5</sub> CAS 541-02-6,

a liquid silicone. Its vapour pressure at 20°C is 0.03 kPa. This product is attractive however it is not free of impact on human health according to studies carried in USA and Denmark [4] and [5]. The use of liquid is still marginal but is growing [8]. For any substitution of current solvents used in dry cleaning, special attention has to be paid to classification of solvents (see chapter 5.1).

There are 4 types of dry cleaning machines presently in operation [1]:

**Machine type I:** this type of machine has only a water cooled unit at a temperature of 20-30°C to condense the solvent. After water cooling, the solvent laden air is exhausted without an activated carbon filter. The emissions to air are about 105 g solvent/kg textiles. The solvent consumption is about 110 g solvent/kg textiles.

**Machine type II:** this type of machine has a refrigeration cooling unit condensing perchorethylene at a temperature of -20°C. The exhaust air passes an activated carbon filter before being exhausted. The emissions to air are about 45 g solvent/kg textiles. The solvent consumption is about 50 g solvent/kg textiles.

**Machine type III:** this type of machine is a closed machine with a closed drying cycle where the drying air is recirculated through a refrigeration cooling unit. There is no exhaust air released. The assumed emissions to air are about 20 g solvent/kg textiles and the range of emissions 20 to 40 g solvent/kg textiles. The solvent consumption is about 25 g solvent/kg textiles.

**Machine type IV:** this type is totally closed with a closed drying cycle similar to type III. In this case, the air stream for drying cycles, circulates through the refrigeration cooling unit and the activated carbon, until the concentration of solvent in the turning cage is below 2 mg/m<sup>3</sup>. The solvent from the adsorption phase of the activated carbon adsorber is returned into the machine. The assumed emissions to air are about 5 g solvent/kg textiles. The solvent consumption is about 10 g solvent/kg textiles.

## 7.33.3 Available Techniques, associated emission levels

#### Wet cleaning

A generally applicable primary measure with a high emission reduction potential consists in switching to wet cleaning processes with water

Wet cleaning use water to clean clothes that are typically dry cleaned. A special detergent and sizing formulated for wet cleaning applications is used. Both products are automatically dispensed to the machine at quantities set by the individual cycle programs. The detergent is a combination of active detergents, glycol ether, anti-shrinking agents, and alcohol dissolved in water. Occasionally, starch and other spot cleaners are used, some of which may contain hazardous chemicals. Wet cleaning is carried out in computer controlled washing and dry machines. The main cross media effect is water pollution. The quality can be lower than with solvent dry cleaning as fabrics can be deteriorated as colours. Restrictions with regard to leather and fabric have to be accounted for.

#### New generation dry cleaning machines

By introducing new generation closed-circuit machines (equipped with a condenser and an activated carbon filter), like type IV machines described above, VOC emissions can be reduced by 95% in comparison to open machines. Conventional closed-circuit machines with activated carbon filters can only reduce emissions by 80%.

Emission source	Combination of control measures	Available Technique Associated Emission Levels for VOCs (yearly average for total AEL)
Open circuit machine and conventional closed machines (type I to type III machines)	Switch to wet processes with water	0 g/kg textiles cleaned
Solvent used : perchlorethylene (PER) or hydrocarbons	Switch to the newest generation type IV machine (closed machine with refrigeration cooling and activated carbon)	5 g/kg textiles cleaned

## 7.33.4 Emerging techniques

#### Liquid CO<sub>2</sub> cleaning

Liquid  $CO_2$  cleaning machines already exist but are not yet widely spread. Like in a conventional process, liquid  $CO_2$  cleaning machines have a cleaning chamber, a circulation loop, a filtration system, a lint trap, a distillation unit and storage. The equipment and chemistry is specially developed to house the pressure and interact with carbon dioxide. Garments have not to be dried after cleaning. Due to its low viscosity, liquid  $CO_2$  enables to clean garments easily. Its performance is comparable to PER. A slight difference in cleaning performance is dirty motor oil and lipstick. However, these stains can be pre-spotted or post-spotted for complete stain removal [6].

#### Water less washing machines

The process is based on the use of plastic granules that are tumbled with the clothes to remove stains. The water consumption of 100 ml/kg garments is very low compared to traditional wet cleaning machines [8].

## 7.33.5 Cost data for emission reduction techniques

Costs are defined in the EGTEI background document concerning dry cleaning [3]. Investment cost of the last generation closed circuit machine is approximately 25 % higher than a conventional closed circuit machine.

## 7.33.6 References used for chapter 7.33

[1] Institute for health and consumer protection European Chemical Bureau. Risk assessment report for tetrachloroethylene. Final report 2005 – EUR 21680 EN

[2] Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[3] EGTEI background document: Dry cleaning - 2005

[4] Siloxanes in the Nordic Environment, TemaNord 2005 : 593 Nordic Council of Ministers, Copenhagen 2005 - ISBN 92-893-1268-8

[5] EPA study on siloxanes

[6] INERIS – rapport d'étude ERSA 05 9 – Note sur les produits de substitution du perchloroéthylène.

[7] Birgit Mahrwald UBA Comments on GD 7-36 dry cleaning version 1

[8] AEA energy and environment, OKOPOL and BIPRO: Guidance on VOC substitution and reduction for activities covered by the VOC solvent emissions directive – Guidance 11 - Dry cleaning – European commission 2008

# 7.34 Surface cleaning

## 7.34.1 Coverage

This chapter covers stack and fugitive VOC emissions from cleaning processes using solvents carried out in industry. The metalworking industries are the major users of solvent cleaning, i. e. automotive, electronic, plumbing, aircraft, refrigeration and business machine industries. Solvent cleaning is also used in activities such as printing, chemical industry, plastic processing, rubber processing, textile processing, mirror manufacturing, paper industry and electric power and solvents are used for paint. Most repair stations for road vehicles and electronic tools use solvent cleaning at least part of the time.

## 7.34.2 Emission sources

Surface cleaning with solvent (often named solvent degreasing) is the process of using organic solvents to remove water-insoluble residues such as grease, fats, oils, waxes, carbon deposits, fluxes and tars from metal, plastic, fibreglass, printed circuit boards and other surfaces.

Several types of degreasing agents for surface cleaning are used:

- organic solvents, halogenated or not halogenated,
- aqueous solutions with use of alkalis, acids, silicates, phosphates and complexing and wetting agents [1],
- supercritical CO<sub>2</sub>,
- biological agents,
- ultrasonic degreasing.

Organic solvents used in degreasing applications, are:

- chlorinated solvents. They are not flammable (no flashpoint) but many of them are classified R40 (perclorethylene and methanedichloride) or R45 (trichlorethylene),
- hydrocarbon solvents or A3 class solvents (flash point larger than 55°C meaning these solvents are not flammable under current uses but can become flammable during non controlled uses (flammable solvents have a flash point < 55° C)),</li>
- alcohols and ketones which are flammable,
- HFC hydrofluorocarbons, HFE hydrofluoroethers, PFC perfluorocarbons used in special cleaning applications such as electronic whose main concern is their potential impact on stratospheric ozone even if their ODP (ozone depletion potential) is low but also climate change (PFC and HFC are green house gases regulated under the Kyoto Protocol). HFE are included in the fourth assessment report of IPCC (AR4) [5].

Solvent cleaning is most often used when the metallic part has to be dried after degreasing.

- The following parameters have a great influence on the choice of the surface cleaning process:
- the medium to be cleaned,
- the type of impurity to be removed,
- the manufacturing process,
- the requirements induced by subsequent process steps.

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The degreasing methodologies surface cleaning techniques can be summarized as followsin the following table:

Table 1: main surface cleaning techniques

Process	Type of machine	Cleaning product used	
	Manual (with a chiffon as example)	Alcohols	
Cold cleaning	Open machines	Chlorinated solvents	
	Closed machines		
	Open top machines		
	Covered open top machines		
	Closed machines	Chlorinated solvents	
	Closed sealed machines		
Hot cleaning	Open top machines		
	Covered open top machines	Hydrocarbons	
	Closed machines		
	Closed sealed machines		
	Mono tank machine,	Alkalis, acids, silicates, phosphates, complexing and	
Aqueous cleaning	Multi tank machines		
	Tunnel machines	wetting agents	

With organic solvents, two types of process exist [1], [2]:

- cold cleaning : cold cleaners are mainly applied in maintenance and manufacturing. They are batch loaded, non-boiling solvent degreasers. Cold cleaner operations include spraying, brushing, flushing, and immersion. In a typical maintenance cleaner, dirty parts are cleaned manually by spraying and then soaking in the tank. After cleaning, the parts are either suspended over the tank to drain or are placed on an external rack that routes the drained solvent back into the cleaner. The cover is intended to be closed whenever parts are not being handled in the cleaner. Typical manufacturing cold cleaners vary widely in design, but there are two basic tank designs: the simple spray sink and the dip tank. Of these, the dip tank provides more thorough cleaning through immersion, and often is made to improve cleaning efficiency by agitation.
- vapour cleaning: vapour degreasers are batch loaded boiling degreasers that clean with condensation of hot solvent vapour on colder metal parts. Vapour degreasing uses halogenated solvents (usually perchloroethylene, trichloroethylene), because they are not flammable and their vapours are heavier than air. A typical vapour degreaser is a sump containing a heater that boils the solvent to generate vapours. Parts to be cleaned are immersed in the vapour zone, and condensation continues until they are heated to the vapour temperature. Residual liquid solvent on the parts rapidly evaporates as they are slowly removed from the vapour zone. Cleaning action is often increased by spraying the parts with solvent below the vapour level or by immersing them in the liquid solvent to flow back into the degreasers are equipped with a water separator which allows the solvent to flow back into the degreaser.

For cold cleaners, bath evaporation can be controlled by covering the bath regularly, by using an adequate freeboard height, and by avoiding excessive drafts in the workshop.

For open-top vapour systems, most emissions are due to diffusion and convection, which can be reduced by covering the bath automatically or manually, by spraying below the vapour level, by optimising work loads, or by using a refrigerated freeboard chillers (which may be replaced, on larger units, by a carbon adsorption device).

Vapour cleaning can be carried out in closed sealed machines.

Hermetically sealed machines

These types of machines prevent direct exposure between the solvent and the atmosphere by a series of interlocks, and by the use of a vapour extraction and/or refrigeration system which recycles the vapour back into the solvent sump. This provides an extremely high degree of solvent containment and reduces fugitive emissions. These machines can work either with chlorinated solvents or with other solvents like A3 class hydrocarbons, HFC or HFE. As an option, the complete cleaning device can be operated under a vacuum. This enables distillation at lower temperatures and allows a permanent control of the vapour emissions [3].

#### Aqueous based cleaning systems

This technique consists of water, detergent and a small amount of solvents, and has been shown to provide a reasonable cleaning efficiency for certain applications. Besides acid cleaning baths, strong till weak alkaline and neutral products are used for industrial cleaning of hard surfaces. Neutral cleaners are predominantly applied for intermediate and final surface cleaning, whereas strong alkaline products aim at obtaining highly cleaned surfaces before surface ennoblement, phosphatation or coating processes. Acid products are found in special applications. Water-based cleaning agents can be used for the cleaning of metals such as steel, aluminium, magnesium, copper, etc., but also for plastics, coated surfaces, glass and electronic parts. In large parts of industrial surface cleaning, water-based systems have been established, leading partly to even better cleaning results as former solvent-based systems. This effect is especially related to further processing of the substrate, such as socating. The two main techniques used in aqueous systems are immersion (small tanks to multi-tanks system) and aspersion (small machines interoperations with complete tunnels).

#### **Biological cleaning process**

This technology is based on a water-based cleaning agent combined with an integrated microbiology for the degradation of oils and grease. The water-based cleaning solution is light alkaline to allow the degreasing of a wide range of metals (e. g. copper, iron, aluminium, zinc). The used micro organisms are natural, their living conditions are optimised and continuously controlled via a computer system in order to keep the determinant parameters of the milieu optimal. In order not to endanger the micro organisms, the cleaning temperature is kept between 40 and 45 °C (but can go down to 35°C in certain systems) and the pH-value must remain around 9. The cleaning agent is regenerated via automatic dosage. When comparing to conventional degreasing processes, the amount of generated waste water is in this case much smaller. Some substances cause damage to the micro organisms, or worse kill them; among these substances are chlorinated products, whose degradation has not yet been clarified. The main applications encountered are degreasing fountains for maintenance cleaning in the cold cleaning application.

## 7.34.3 BAT, Associated Emission Levels (AEL)

General emission reduction options in this sector are [1]:

- minimisation of the amount of grease and oil, selection of oils greases or systems that allow the use of the most environmentally friendly degreasing systems
- mmprovement of equipment:
  - cold cleaning : systematic use of covers, reduction of pulverisation pressure,
  - vapour degreasing : systematic use of closed sealed machines for vapour degreasing with chlorinated solvent, hydrocarbons or other solvents such as HFE, HCFC and PFC
  - Higher freeboards for the reduction of organic solvent losses for degreasing baths; refrigerated freeboards for degreasing baths associated with activated carbon adsorption.
- substitution of solvent based cleaning agents:

all solvents such as trichloroethylene which are classified as carcinogenic compounds, have to be substituted if not used in safe and hermetically sealed machines.

- vapour degreasing : use of aqueous based cleaning agent (using also the BAT defined for these processes [1]),
- cold cleaning : biological agents, use of fatty acids of natural or synthetic esters [3].
- regeneration of used organic solvents on-site or by an external regenerator;

• switch to low-temperature plasma processes (still using some organic solvent).

Examples of emission reduction measures and performances in surface cleaning are presented in table  $\frac{42}{2}$ 

Table <u>42</u>: emission sources and selected VOC control measures with associated emission levels for surface cleaning [2]

Emission source	Available techniques	Associated emission levels for VOCs
		(yearly average for total AEL)
Vapour cleaning using	Water-based degreasing systems	0 g/kg solvent used*
halogenated solvents or hydrocarbons	Hermetically sealed machines	Less than 0.1 % solvent used*

\* sum of I1 the quantity of organic solvents or their quantity in preparations purchased which are used as input into the process in the time frame over which the mass balance is being calculated and I2 the quantity of organic solvents or their quantity in preparations recovered and reused as solvent input into the process. (The recycled solvent is counted every time it is used to carry out the activity).

## 7.34.4 Emerging techniques

#### Supercritical CO<sub>2</sub>

The principle of this technique is that at supercritical conditions (beyond 75 bars and  $35^{\circ}$ C), intermediary between liquid and gas, CO<sub>2</sub> has solvent properties which have the advantage to be adjustable with the variation of temperature and pressure. This clean solvent is easily recoverable in making it passing again in a gas stage at the end of the cycle. Nevertheless its cleaning power is limited: it works well for non-polar products but is less efficient with polar products. This difficulty can be surmounted by adding few percent of co-solvent or using an ultra-sonic mechanical effect.

#### Plasma degreasing

This technology is already applied in some specific production sectors and can be applied to a large variety of substrates leading partly to even better cleaning results than former solvent systems. This effect is especially related to further processing of the substrate, such as coating of certain plastics with water-based paints. Thus, a double emission reduction may be achieved in some cases. Within the plasma degreasing process, surface cleaning is carried out at temperatures below 100 °C and a pressure between 0.1 and 2.10<sup>-3</sup> hPa. The vacuum chamber is filled with process gas, such as noble gases (e. g. argon, helium), fluorine containing gases (e. g. tetrafluoromethane) or oxygen. An electric field conveys energy to the system, resulting in ionised gas particles. Oxygen is mostly used as process gas. Radicals generated via excitation aim at cutting the hydrocarbon chains and oxidise them to form carbon dioxide and water. The cleaning effect of the plasma is based on this chemical reaction. Organic impurities can be removed by this degreasing process, but plasma technique is not adapted to inorganic impurities such as shavings, mineral dust or salts.

# 7.34.5 Cost data for emission reduction techniques

Costs are defined in the EGTEI synopsis sheet concerning "surface cleaning" [2]. Costs range from 0.4 to  $56 \in / \text{kg}$  VOC abated in the smallest installation and from -0.3 to  $2.97 \notin / \text{kg}$  VOC in the largest one.

# 7.34.6 References used for chapter 7.34

[1] European commission BREF for the surface treatment of metals and plastics - August 2006

[2] EGTEI synopsis sheet: Surface cleaning - 2005

http://www.citepa.org/forums/egtei/27-Synopsis-sheet-surface%20cleaning-30-09-05.pdf

[3] Biosolvants - Enjeux et opportunités - 27 mai 2008 - ADEME

[4] AEA energy and environment, OKOPOL and BIPRO: Guidance on VOC substitution and reduction for activities covered by the VOC solvent emissions directive – Guidance 4/5 – Surface cleaning – European commission 2008

[5] A compilation of technical information on the new GHG gases and groups included in the Fourth Assessment Report (AR4) of the Intergovernmental Panel on Climate Change <a href="http://unfccc.int/national\_reports/annex\_i\_ghg\_inventories/items/4624.php">http://unfccc.int/national\_reports/annex\_i\_ghg\_inventories/items/4624.php</a>

# 7.35 Vegetable oil and animal fat extraction and vegetable oil refining

#### 7.35.1 Coverage

Activities covered relate to the vegetable oil and animal fat extraction and vegetable oil refining activities. The definition is as follows [1]: Any activity to extract vegetable oil from seeds and other vegetable matter, the processing of dry residues to produce animal feed, the purification of fats and vegetable oils derived from seeds, vegetable matter and/or animal matter.

However, presently, due to the problem of bovine spongiform encephalopathy, the solvent extraction of animal fat from dead cows and other animals, for producing animal meals is not more carried out according to [4]. This chapter consequently covers only vegetable oil extraction.

# 7.35.2 Emission sources

The production of crude vegetable oil from oilseeds (e.g. soya beans, sunflower seeds or rapeseed) is a two-stage process:

• the first process step is cleaning, preparation (i.e. drying) and in some cases dehulling, flaking and conditioning and pressing of the oilseeds. Pressing takes place in one or two steps, resulting in crude pressed oil and a cake.

Beans (with 20% oil or less) are not pressed, because of the lower fat content, but are extracted directly after cleaning and preparation.

 the second process step is the extraction of oil from the pressed cake or flaked beans using hexane as a solvent. Extraction takes place in counter-current flow desolventiser-toaster (DT) by means of direct or indirect steam.

The mixture of hexane and oil, called miscella, is further processed in a distillation process, to separate the hexane from the vegetable oil. The solvent is re-used in the extraction process. Oil is further refined to become consumable.

The hexane remaining in the cake is recovered by a stripping process, using steam. This desolventising-toasting process also reduces the enzyme and micro organism activity in the meal.

The meal is dried and cooled by air before storage in silos or before loading.

Refining consists in several operations which can be physical or chemical. Conventional chemical refining includes degumming for the removal of phospholipids, neutralization for the removal of free fatty acids (ffa) and bleaching for decolourisation and deodorization.

VOCs emissions arise from the oil extraction process. Fugitive and stack emissions occur. The refining process is not the main source of VOC emissions however VOC emissions arise from the neutralisation and the deodorisation steps. Dust emissions arise from the drying of desolventised and toasted meals. Excess moisture in removed by heated ambient air and after, by cooled ambient air. The exhaust air contains dusts [3].

## 7.35.3 BAT, Associated Emission Levels (AEL)

For the extraction of vegetable oil and the refining of vegetable oil, several VOC emission reduction options are available.

Batch and continuous processes are to be distinguished in terms of emission relevance, the former are more relevant. By introducing the so-called Schumacher-type desolventizer-toaster-dryer-cooler in the edible and non-edible oil extraction sector, VOC emissions can be reduced significantly.

For reducing emissions, several techniques can be used [2] and associated and are constituted of:

Process optimisation: the counter current flow Desolventizer-Toaster (DT) allowing to minimize the solvent losses and steam consumption, the heat integration of DT vapour stream with miscella

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distillation in the extraction process leading to an optimisation of the energy consumption, the mineral oil scrubbing system to reduce VOC emissions and the reboiler minimising solvent losses.

Use of secondary measures by Condensation/Physical Separation/Distillation: the hexane and steam vapours coming from the meal desolventising/toasting, from the miscella (crude vegetable oil and hexane) distillation, from the reboiler and from the stripping column of the mineral oil system, all pass through a condenser system. The condensed vapours (hexane-water condensate) go to the hexane-water separator where the undissolved hexane is separated by means of gravitational phase separation. The hexane is re-circulated to the extraction process. Any residual solvent content in the aqueous phase of the hexane/water separator is distilled off in the so-called re-boiler. The resulting hexane/water vapours from the reboiler are condensed together with the vapours from the distillation stage.

After boiling the almost hexane-free water is fed to the waste water system. This technology also ensures the explosion safety of this downstream system.

#### Use of secondary measures by Absorption/Desorption

The components that cannot be condensed by the condenser are treated further by an absorption technique, the so-called mineral oil scrubbing system, where residual hexane is absorbed. The mineral oil system consists of an absorption column, where the hexane is absorbed by cold, food grade mineral oil. The hexane is then recovered by steam stripping the hexane laden mineral oil in a stripping column. The stripped mineral oil is cooled down and reused in the absorption column.

The final emissions from the mineral oil system consist of the non-condensables with traces of hexane.

The hexane and steam vapour from the mineral oil stripping column are condensed in the condenser system. The hexane-water condensate then goes to the hexane-water separator (see above). The total recovered hexane is reused in the extraction process.

Dusts are removed by cyclones for safety reasons. The use of fabric filters and electrostatic precipitators increase the fire hazard and cannot be used.

BAT for this sector is consequently to [3]:

- use of a counter flow desolventizer toaster (Schumacher type as example)
- use the vapour generated in the desolvantiser toaster in the first step of the miscella distillation pre-evaporator,
- use water ring pumps to generate an auxiliary vacuum for oil drying, oil degassing or minimising oxidation of oil,
- use a mineral oil scrubber to recover hexane from incondensable vapours from meals desolventising toasting, miscella distillation, the reboiler and from the stripping column of the mineral oil system,
- use cyclones to reduce wet dust emissions arising from vegetable oil extraction, to achieve a wet dust emission level of less than 50 mg/Nm<sup>3</sup>,
- better control deviations from normal operating conditions and avoid start-ups and shut-downs
   [2] (this is however depending on the number of different types of seeds to treat in the year and much more difficult if this number high).

[Achievable emission levels were defined in the EGTEI background document assuming biofiltration use. However, according to FEDIOL, biofiltration is not feasible due to the very limited water solubility of hexane. The achievable emission level given in the previous Gothenburg Protocol guidance document III has also been modified according to data defined in the EGTEI background document [2]].

Table 1: control measures with VOC associated emission	on levels for extraction of vegetable oil
Table 1. control measures with VOC associated emission	on levels for extraction of vegetable on

	Emission source	Combination of control measures	BAT associated emission levels for VOC [Defined for the following averaging period: (yearly averagefor total AELfor total AEL)]
I	Extraction of oil from seed, continuous process from rapeseeds, sunflower seeds and soya beans.	Process optimization and counter flow desolventizer-toaster-dryer-cooler and condensation with further absorption (mineral oil scrubbing system) and other techniques	0.5 g/kg seed processed [2]
	Extraction of oil from other seeds such as safflower seed, mustard seed, cotton seed and vegetable material	described above	3 g/kg seed processed <del>[as in [</del> 3] <del>]</del>
	Extraction of seeds in batch process		4.0 g/kg seed processed
	All fractionation processes : excl. degumming: Degumming:		1.5 g/kg seed processed
			4.0 g/kg seed processed <del>[as in [</del> 3] <del>]</del>

## 7.35.4 Cost data for emission reduction techniques

Costs have been defined in the EGTEI documents [2]. Abatement costs defined are negative as investments lead to hexane consumption reduction.

Caution: these documents are susceptible to evolve if new updated data are available.

# 7.35.5 Emerging techniques

No data is available.

## 7.35.6 References used in chapter 7.35

[1] Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[2] EGTEI background document/synopsis sheet: Fat edible and non-edible oil extraction – 2003/2005

[3] European Commission - reference document on BAT for the food, drink and milk industries \_\_ August 2006

[4] M. GESLIN from National federation of fat compounds (Fédération Nationale des Corps Gras) – Information to CITEPA – September 2008

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# 7.36 Vehicle refinishing

#### 7.36.1 Coverage

This sector covers the coating of road vehicles, or part of them, carried out as part of vehicle repair, conservation or decoration outside manufacturing installations as considered in annexe IX.

Vehicle refinishing comprises coating and surface cleaning activities.

## 7.36.2 Emission sources

The main VOC emission sources in this sector are the application of paint, the drying operations, the cleaning of equipment, and the cleaning operations before the coating and between the applications of different layers.

#### 7.36.3 Available techniques, Achievable Solvent Concentrations

Emission reduction can be achieved by primary measures such as good housekeeping, low organic solvent containing paints (including water-based systems), high-volume, low-pressure (HVLP) guns, and gun cleaning devices. Secondary measures are normally not applicable for economic and efficiency reasons.

The maximum VOC contents permitted under the Product Directive 2004/42/EC are defined by product category in table 1 below.

Product Subcategory <sup>1</sup>	Coatings	VOC (g/l) <sup>2</sup>
Preparatory and cleaning	Preparatory	850
	Pre-cleaner	200
Bodyfiller/stopper	All types	250
Primer	Surfacer/filler and general (metal) primer	540
	Wash primer	780
Topcoat	All types	420
Special finishes	All types	840

#### Table 1: achievable solvent concentrations for each type of paint

<sup>1</sup> Product subcategories are defined in annex XI

<sup>2</sup> g/l of ready for use product. Except for "preparatory and cleaning", any water content of the product ready for use should be discounted.

#### 7.36.4 Cost data for emission reduction techniques

Abatement costs corresponding to the respect of the Directive 2004/42/CE are about 1,400  $\in$ /t VOC abated. The detailed methodology used to estimate these costs is defined in the EGTEI synopsis sheet concerning "vehicle refinishing" [1].

Caution: this document is susceptible to evolve if new updated data are available.

## 7.36.5 Emerging techniques

Further reductions seem to be possible.

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## 7.36.6 References used for chapter 7.36

[1] EGTEI synopsis sheet: Vehicle refinishing - 2005

[2] Directive 2004/42/EC of the European Parliament and of the Council of 21 April 2004 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in decorative paints and varnishes and vehicle refinishing products and amending Directive 1999/13/EC

## 7.37 Wood impregnation

## 7.37.1 Coverage

This sector covers the wood impregnation in organic solvent-based preservatives, creosote and waterbased preservatives. Wood preservatives may be supplied for both industrial and domestic use. Only industrial applications are treated in this section.

## 7.37.2 Emission sources

Wood is preserved to protect it against fungal and insect attack and also against weathering. Different types of preservatives are used [1]:

- solvent-based preservatives: traditional preservative systems consist of approximately 10% active ingredient and 90% organic solvents, usually whit spirit or other petroleum-based hydrocarbons. Without additional measure, the reference VOC emission is about 19.8 kg/m<sup>3</sup> of wood treated, concentrated pesticide systems: these are solvent-based solutions with a higher concentration of pesticides,
- water-based preservatives: they consist of solutions of salts in water. VOC emission reductions above 99% are observed compared to the reference situation,
- creosote: it is an oil prepared from coal tar distillation. Approximately 10% of the creosote used for wood preservation is made up of VOC.

The estimation of emissions can either be based on the quantity of preservatives consumed or on the quantity of timber treated.

The application of the preservative may be carried out via vacuum processes, pressure processes, dipping, spraying or brushing. The vacuum process may vary slightly, depending on the preservative product. The application efficiency of the pesticide for dipping and brushing is close to 90% and using the vacuum process with full containment is close to 100%. Spraying has a much lower efficiency, i.e. from 5 - 50%.

## 7.37.3 BAT, Associated Emissions Levels (AEL)

According to the STS BREF [1], it is BAT to use a vacuum impregnation with water-based or high concentration pesticide solvent systems or waste gas treatment such as activated carbon or condensation. 99% reduction can be achieved using water-based systems and 70% with solvent-based systems and waste gas treatment (about 15 to 25% of the solvent remains in the wood and evaporate over the life of the product).

As a significant amount of solvent is released after the wood has been treated, it is BAT to use solvents with lower ozone-forming potentials.

Techniques and corresponding associated emission factors defined in the table below originate from the EGTEI background document [2].

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Table 1: emission sources and selected VOC control measures with associated emission levels for impregnation of wooden surfaces

Emission source	Combination of control measures	BAT associated emission levels for VOC [2] [Defined for the following averaging period:( yearly average for total AEL)]
All installations	100% of solvent based preservatives vacuum impregnation system and waste gas treatment such as activated carbon or condensation* (adsorption on cartridges with off-site recovery or disposal may also be considered)	~ 6 kg/m <sup>3</sup> wood treated
	Process optimisation 100% of more concentrated solvent based preservatives vacuum impregnation system	11 kg/m <sup>3</sup> wood treated
	100% of water based preservatives vacuum impregnation system	~ 0.2 kg/m <sup>3</sup> wood treated

\* According to the STS BREF [1], treatment of emissions is carried out in large installations when, in small plants, abatement equipment may not be economically viable.

## 7.37.4 Cost data for emission reduction techniques

Costs and methodologies are defined in the EGTEI documents concerning "preservation of wood" [2].

Abatement costs for primary measures vary from 0.3 to 0.7 k€/tonne of VOC abated and are even negative in some particular cases. When secondary measures are implemented, abatement costs vary from 1 to 21 k€/tonne of VOC abated depending on the size of the installation and on the technique used.

Caution: these documents are susceptible to evolve if new updated data are available.

## 7.37.5 Emerging techniques

No data is available.

## 7.37.6 References used for chapter 7.37

[1] STS BREF – August 2007

[2] EGTEI background document/synopsis sheet: Wood preservation - 2004/2005

# 7.38 Solvent content in products 2: Domestic uses of solvent (other than paints)

## 7.38.1 Coverage

This source category covers the domestic application of glues, use of car care products, cleaning agents, leather and furniture care products, pesticides, and cosmetics and pharmaceuticals.

## 7.38.2 Emission sources

VOC emissions are due to the solvents contained in the products. All solvents used are considered to be 100% emitted into the atmosphere.

## 7.38.3 Available techniques, Achievable Solvent Concentrations

For the domestic use of organic solvents, emission reduction options are given only in terms of substitution by zero or low organic solvent containing products (mainly water-based products), by non-organic propellants, and the reduction of the packaging volume.

The BIPRO study aiming at identifying reductions in VOC emissions from the use of product [1] defines maximum VOC content which could be mandatory in a list of products. 3 types of products are considered: propellants, cosmetics (besides aerosols) and adhesives used outside installations (which are already covered by the Directive 99/13/EC [2]). Maximum allowed VOC content are presented in the table below.

The most important emission sources from the use of products containing VOC in the EU are [1]:

<ul> <li>aerosol in cosmetics (propellants)</li> </ul>	180 kton/a
- solvents in cleaning products	110 kton/a
- solvents in adhesives	100 kton/a

Table 1: maximum allowed VOC content for each type of domestic products

	Maximum allowed VOC content [%]	ELV from the Californian regulation [1], [3]
Propellants		
Hair sprays	75	55
Deodorants	20	10
Antiperspirants	75	10 (MVOC), 40 (HVOC)
Cleaning Agents	10	4
Cosmetics (besides aerosols)		
Skin care products	20	
Shampoos, soap and bath products	3	
Shaving products	3	
Flagrances	80	75
Deodorants	20	10
Adhesives used in building and const	truction	
Roofing	Solvent free a/	
Insulation	Solvent free <sup>a/</sup>	

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	Maximum allowed VOC content [%]	ELV from the Californian regulation [1], [3]
Ceiling titles	30	
Plywood paneling	Solvent free <sup>a/</sup>	
Floor covering	8 <u>a/</u>	
Adhesives in woodworking and joiner	'y	
Wood	Solvent free a/	
Varnished surfaces	No limitation <sup>b/</sup>	
Leather, textiles, felt	8 <u>a/</u>	
Rubber, plastics, PVC	70 <sup><u>b/</u></sup>	
Cushions and foams	8 <u>a/</u>	
Adhesives for footwear and leather		
Shoe upper assembly	10 <sup><u>a/</u></sup>	
Sole assembly	55	
Sole fitting	No limitation	
Adhesives used by consumers, DIY		
Wood	Solvent free	
Paper and board	Solvent free	
Multipurpose and contact adhesives	No limitation <sup>b/</sup>	
Modelling and plastics	70 <sup><u>b/</u></sup>	

a/ exceptions for specific applications

b/ use of alternatives dependant on material and technical conditions

## 7.38.4 Cost data

No data is available.

## 7.38.5 Emerging techniques

No data is available.

## 7.38.6 References used for chapter 7.38

[1] Screening study to identify reductions in VOC emissions due to the restrictions in the VOC content of products

[2] Directive 1999/13/EC of 11 March 1999. on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

[3] Regulation for reducing VOC emissions from consumer products, Title 17, California Code of Regulations, Division 3, Chapter 1, Subchapter 8.5, Article 2, Consumer Products, Sections 94507-94517 (dec. 2007).

## 7.39 Beer production

## 7.39.1 Coverage

Breweries with a production capacity of 300 tonnes finished product per day are covered by this section on beer production. Here, the sector of beer production includes the malting stage, even though these two process steps are carried out in different locations [1], [2].

#### 7.39.2 Emission sources

Cereals used in the production of beer and some spirits are usually allowed to germinate before use. This process is called malting, and results in the conversion of starch into sugars. Germinated cereals may then be roasted. The length of roasting varies depending on the type of grain and the type of beverage to be produced. Before fermentation, cereals are often boiled in water to produce wort, which is then filtered to separate out the solid residues.

Fermentation occurs in large fermenting vessels and typically lasts one to three weeks. Normally, vessels are sealed, recirculating the carbon dioxide. Others, normally in smaller plants, vent to atmosphere via a water trap [3].

## 7.39.3 BAT, Associated Emission Levels (AEL)

In order to reduce energy consumption, BAT for breweries is to reuse hot water from wort cooling, recover heat from wort boiling and from condensing vapours (this also reduces odour emissions) to preheat the next batch or process water. Where applicable,  $CO_2$  should be recovered by cleaning, compressing, drying and purifying it from the beer fermentation gas [1], [2], [4].

#### 7.41.1.1 SO<sub>2</sub>

As a measure to reduce  $SO_2$  emissions, it is recommended to use commercially available low-sulphur fuels [5].

However,  $SO_2$  emissions are not considered to be very significant for the sector of beer production and are not discussed further; information on emissions from energy generation can be found in the part on industrial boiler plants.

## 7.41.1.2 NOx

As a measure to reduce  $NO_{\chi}$  emissions, the use of low  $NO_{\chi}$  burners and regular maintenance of the boiler is recommended [5].

However, these emissions are not considered to be very significant for the sector of beer production and are not discussed further; information on emissions from energy generation can be found in the part on industrial boiler plants.

## 7.41.1.3 Dust

If necessary, cyclones, fabric filters or electrostatic precipitators should be used on exhaust air to remove particulates [3], [5].

However, these emissions are not considered to be very significant for the sector of beer production and are not discussed further; information on emissions from energy generation can be found in the part on small combustion plants  $[6]^{\frac{1}{2}}$ .

According to the EMEP/Corinair guidebook 2006 : "These activities are not believed to be a significant source of PM<sub>25</sub> (as of December 2006) Mis en forme : Police :8 pt Mis en forme : Anglais (États Unis)

[comment: Corinair 2006 : "These activities are not believed to be a significant source of PM<sub>2.5</sub> (as of December 2006)"]

## 7.41.1.4 VOC

Beer production is generally responsible for odorous emissions. Considerable emissions of VOCs can be released from larger breweries, appropriate abatement techniques for odour and VOC should be used and exhaust gases should be reused where possible. VOC emissions are partly controlled as a result of odour reduction requirements and can be reduced by working in closed cycles, e.g. by  $CO_2$  recirculation. If the exhausted air from the brewhouse is condensed and the gas from fermentation is recovered, there is no need for further emission abatement like biofiltration. If not, Biofiltration is a very useful control measure and is particularly suitable for low VOC concentrations in the exhaust air and for odorous emissions. Biofilters reduce odour and VOC emissions by absorbing the pollutants onto the filter material and degrading them by the microorganisms located on the fixed filter medium. They are applicable for a wide range of airflows (up to >100000 m<sup>3</sup>/h), but airborne temperature may not exceed 40°C. The investments and operating costs of biofiltration in this case are lower than those of conventional control techniques (e.g. activated carbon adsorption). Alternatively, the organic odour components can be removed by condensing the vapour from boiling vessels combined with energy recovery.

VOC emissions generated by certain process steps may be reduced by applying control techniques like condensation, activated carbon adsorption, or incineration. Selected applicable abatement options and their respective achievable emission factors are given in Table 1 for beer production [1], [2], [4].

	Emission source	BAT associated emission levels <sup>1</sup> <del>mg/Nm<sup>3</sup>-or (kg/tonne)</del> kg/m <sup>3</sup> <u>beer</u>	Comments
	Beer production (capacity > 1,000 m³/year)	<del>(</del> 0.004) <del>[kg/m<sup>3</sup> beer] [2]</del>	Condensation of exhaust air from the brewhouse and recovery of fermentation gas or Biofiltration of emissions from the malting of grain and CO <sub>2</sub> recovery during fermentation
			[comment: EMEP/Corinair guidebook 2007 : 0.035 kg/hl beer; no value given in BREF]

#### Table 1: VOC emission levels associated with BAT for beer production [2]

<sup>1</sup> The BAT associated emission levels are based on a daily average, standard conditions and represents a typical load situation. For peak load, start up and shut down periods, as well as for operational problems of the flue gas cleaning systems, short-term peak values, which could be higher, have to be regarded.

#### 7.41.1.5 Cross Media Effects

For all mentioned emission reduction and abatement techniques, the cross-media transfer of pollutants and the full range of environmental effects and improvements should be considered. For example additional energy consumption and increased quantities of waste or wastewater residuals may result from individual efforts for pollutant prevention, reduction, or removal.

## 7.39.4 Emerging Technologies

No major technological breakthroughs are expected for this sector.

## 7.39.5 Cost data for emission reduction technologies

## 8 Table 2: cost data for CO<sub>2</sub> recovery and biofiltration [1]

Characteristics of reference installation	Control options	Investments <sup>a/</sup> [EURO]	Operating costs <sup>⊵⁄</sup> [EURO/year]	Abated mass flow [Mg VOC/year]
Beer production (malting included)				
Large brewery; production capacity: 150,000 m³/year beer; operating time: 4,000 h/year	CO <sub>2</sub> recovery during fermentation and biofiltration of emissions from malting of grain	250,000	3,2000	9

VP: vapour pressure.

a/ Depending on e.g. waste gas flow rate, VOC concentration in the waste gas, production capacity. Unless specified otherwise, all investments mentioned represent additional investments if the technology switch occurs in the course of an autonomous technology change.

b/ Depending on e.g. waste gas flow rate, VOC concentration in the waste gas, heat recovery rate.

## Table 32: cost data for biofilters [1]

Installation size (airflow)	Specific investment	Operating cost
Small (200-500 m <sup>3</sup> /h)	45-50 €/m³	
Larger plants	Down to 10-15 €/m³	0.225-0.3 €/1000m³ (including 0.15-0.225 €/1000m³ energy cost, calculated with electricity costs at 0.15 €/kWh)

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## 7.39.6 References used in chapter 7.39

2 Old version of the Gguidance document on control techniques for emissions of sulphur, NOx and VOCs from stationary sources - 1999

4 IFC 2007. International Finance Corporation (World Bank Group): Environmental, Health, and Safety Guidelines for Breweries

5 The Brewers of Europe 2006: Guidance Note for establishing BAT in the brewing industry

6 EMEP/CORINAIR Emission Inventory Guidebook (Activities 040606-040608), December 2006

<sup>1</sup> European Commission. 2006: "Integrated Pollution Prevention and Control (IPPC) Reference Document on Best Available Techniques in the Food, Drink and Milk Industries." http://eippcb.jrc.es/pages/FActivities.htm

<sup>3</sup> Environmental Protection Agency Ireland. 2006: Draft BAT Guidance Note on Best Available Techniques for the Brewing, Malting & Distilling Sector (Final draft)

## 7.41 New Stationary Engines

## 7.41.1 Coverage

The stationary engines sector covers combustion techniques of stationary engines using liquid or gaseous fuels. This paper focuses mainly on reduction of nitrogen oxide emissions (NO<sub>x</sub>) from new stationary engines with a rated thermal input of more than 1 MW<sub>th</sub> spark ignition (SG) or dual fuel (DF in gas mode) or more than 5 MW<sub>th</sub> diesel engines. Some information is also given on the effects of fuels and reduction of dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC), carbon monoxide (CO) and volatile organic compound (VOCs) emissions from stationary engines (definitions are provided in chapter 1, 5 and 6).

#### 7.41.2 Combustion technologies

The combustion processes as a whole lead to the generation of emissions to air, which are considered to be one of the major sources of air pollution. Depending on the type of the fuels and techniques available, several technologies (such as boilers, gas turbines or stationary engine plants) are available which show considerably different  $NO_x$ ,  $SO_x$  and particulate matter emissions. This paragraph describes the main stationary engine technologies used for the combustion of liquid and gaseous fuels.

Definitions for engines:

Stationary engines can be divided according to fuel used into (see Table 2):

- diesel engines (inclusive dual fuel high pressure gas diesel (GD))
- spark plug or by other device ignited gas engines (SG) and
- dual fuel engines (low pressure gas DF).

Also, stationary engines can be divided into 2- and 4-stroke engines-

- 2-stroke engines with compression or open chamber ignition and combustion are low speed engines (<300 rpm) and can be either one or (high pressure gas) dual fuel (GD) solutions.</li>
- 4-stroke engines are ignited with compression, pilot, spark or hot body principle, they have open chamber, pre-chamber, lambda 1 or lean-burn combustion solutions and are either medium (300 < n < 1200 rpm) or high speed (> 1200 rpm) engines. Different engine solutions are such as gas-fired spark ignited (SG), dual fuel low pressure gas (DF) or high pressure gas diesels (GD) or liquid fired diesel or DF engines.

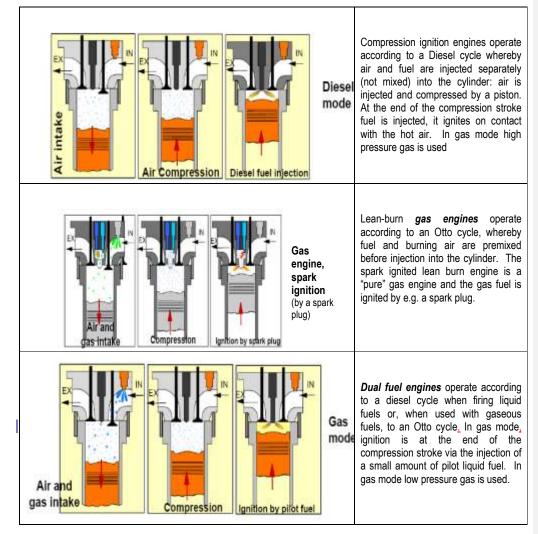
Also, stationary engines can be divided according to their speed:

- the low-speed and medium-speed engines are often used in e.g. base load, decentralized small/medium sized combined heat and power (CHP), gas compression and crude oil pumping and grid peaking plant applications. Low and medium speed engines can operate either in one or dual fuel principle.
- low speed 2-stroke engines (available up to about 90 MW<sub>e</sub> unit sizes) operate on liquid distillate fuel oil, HFO (heavy fuel oil), residual, emulsified fuel oil, refinery vacuum residuals and high pressure natural gas (GD type).
- medium speed 4-stroke engines (available up to about 25 MW<sub>e</sub> diesel engines), up to about 17 MW<sub>e</sub> low pressure gas dual fuel (DF) and spark ignition (SG) up to about 10 MW<sub>e</sub> unit sizes) operate on liquid distillate fuel oil and HFO (diesel and dual fuel engines), liquid residual fuel oil, emulsified fuel oils, refinery vacuum residuals (diesel engines), natural gas (gas diesel (GD), dual fuel (DF) and spark ignition (SG) types), biogas, mining and landfill gas (depending on SG and GD types).
- high-speed engines are mostly used in peak load applications. High-speed stationary engine types
  are usually small (unit size output up to a 5 MW<sub>e</sub>) and mostly operate on natural gas, biogas, landfill

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gas, liquid bio-fuels and liquid distillate fuel oil. High-speed engines are used both in electricity production and in other non-road applications.





Operating principle	Ignition and combustion	Typical classification of engines based on engine speed	Mode of operation	Fuels	Unit electric power output
2-stroke	Compression & Open chamber	Low speed (< 300 rpm)	One fuel operation Dual fuel (GD) (high pressure natural gas)	Liquid distillate fuel (diesel oil), HFO, residual, emulsified fuel oil, <i>refinery vacuum residuals,</i> <i>natural gas</i>	Up to 90 MW <sub>e</sub>
4 –stroke	Ignition -Compression -Pilot -Spark -Hot body <u>Combustion</u>	Medium speed (300 – 1200 rpm)	One fuel operation Liquid fuels, gas (Spark ignited type, SG) Dual fuel operation High pressure natural gas (Gas Diesel, GD) Low pressure natural gas (Dual Fuel, DF) Back-up-mode: liquid fuel	Chapter 2): Liquid distillate fuel (diesel oil), HFO, liquid residual fuel oil, emulsified fuel oils, refinery vacuum residuals, liquid	Up to - 25 MW <sub>e</sub> (diesel) - 17 MW <sub>e</sub> (DF) - 10 MW <sub>e</sub> (SG)
	-Open chamber -Pre-chamber -Lambda 1 -Lean-burn	High speed (> 1200 rpm)	One fuel operation Liquid fuels, gas (Spark ignited type)	Natural gas, biogas, landfill gas, liquid biofuels, liquid distillate fuel oil (diesel oil),	Up to 5 MW <sub>e</sub>

 Table 2: current main types of stationary reciprocating engines

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#### BAT for controlling NO<sub>x</sub> emissions from lean burn type gas engines

For gas-fired stationary engine plants, the lean-burn approach to reduce  $NO_x$  emissions is BAT, it is analogous to the dry low  $NO_x$  technique used in gas turbines. This is a primary measure that requires no extra reagents or water additions to achieve low  $NO_x$  levels. For spark plug or by other device ignited (SG) natural gas fired lean-burn engines, a  $NO_x$  level of 95-190 mg/Nm<sup>3</sup> at 15%  $O_2$  and 190-380 mg/Nm<sup>3</sup> at 15%  $O_2$  for low pressure gas dual fuel engines are achievable by primary measures.

Because gas engines can be equipped with a SCR this is also considered as BAT. For engines using natural gas oxidation catalysts are BAT for CO emissions control. Fuel gas cleaning will be needed in most cases<sup>1</sup> when using oxidation and SCR catalysts when burning other gaseous fuels, such as biogas or landfill gases, that might contain catalyst poisons<sup>2</sup>. Engine optimization is a compromise between NO<sub>x</sub> emissions, engine efficiency (fuel consumption and thus CO<sub>2</sub> emission) and other emissions (such as CO and hydrocarbons). With the application of SCR (secondary measure) NO<sub>x</sub> emissions levels in range of 5<sup>3</sup> -19 mg NO<sub>x</sub> /Nm<sup>3</sup> in 15 % O<sub>2</sub> have been measured.

#### BAT for controlling NO<sub>x</sub> emissions from liquid fuel-fired (diesel) engines

The application of primary methods and secondary measures, in particular the application of the SCR system is regarded as BAT to reduce  $NO_x$  emissions from liquid fired diesel engines. A limitation for the applicability of SCR is given for diesel engines, which need to be operated in varying loads. SCR is a commonly applied system for diesel engines but cannot be seen as BAT for engines with frequent load variation due to technical constrains (see LCP BREF p. 406). A SCR unit would not function effectively when the operating conditions and the consequent catalyst temperature are fluctuating frequently outside the necessary effective temperature window. Achievable  $NO_x$  emission levels for operational diesel engines, using primary measures, have been found to range from 1460 to 2000 mg  $NO_x$  /Nm<sup>3</sup> depending on the fuel and engine type. For new engines according to the new IFC/WB Guidelines, depending on bore size, the range of the emission level is 1460 – 1850  $NO_x$  /Nm<sup>3</sup> at 15 %  $O_2$ .

For diesel engines it is necessary to use SCR as a secondary measure to reach the emission limit values of 190 or 225 mg NO<sub>x</sub> /Nm<sup>3</sup> in 15 % O<sub>2</sub> (equivalent to 500-600 mg NO<sub>x</sub> /Nm<sup>3</sup> in 5 % O<sub>2</sub> given in the Gothenburg Protocol. It should be noted that, for engines with SCR, a minimum flue-gas temperature (dependent on the fuel sulphur content) is needed to prevent salt formation clogging the catalyst and that the supply infrastructure is in place to supply ammonia or urea of adequate quality. Achievable NO<sub>x</sub> emission levels with SCR based on the examples of diesel engine plants in operation range from 145 to 325 mg NO<sub>x</sub>/Nm<sup>3</sup> with fuels from light to heavy fuel oils, respectively (EU LCP BREF Table 6.23 and 6.12). It should be noted that the NO<sub>x</sub>-reduction of a SCR system is dependent on the fed reagent amount (dependent on the exhaust gas flow and inlet NO<sub>x</sub> concentration/set outlet NO<sub>x</sub>-limit). The control system will adjust the reagent flow to the SCR based on the feed-forward signal from the engine loading (preprogrammed parameters during the commissioning of the plant based on NO<sub>x</sub> measurements). In some cases also a feed-back signal (from a NO<sub>x</sub>-measurement device) is used for "fine tuning" of the system besides the feed-forward signal. The set NOx-levels various in different countries as the following examples show:

- in Belgium and in the Netherlands  $NO_x$  emission values of 130 to 150 mg/Nm  $^3$  (15  $\%~O_2)$  for new diesel engines have recently been introduced

- according to the German TA-LUFT 2002 the set  $NO_x$ -limit is equivalent to 190 mg/Nm<sup>3</sup> (15 %  $O_2$ ) and the French  $NO_x$ -limit is close to former TA-LUFT 1986 about 750 mg/Nm<sup>3</sup> (15 %  $O_2$ ).

<sup>&</sup>lt;sup>1</sup> Only limited experience exists thus far

<sup>&</sup>lt;sup>2</sup> The catalysts might get deactivated. There is limited experience from SCR with the use of biogas at the moment and the systems are expensive. Additional fuel gas purification equipment is necessary to clean out detrimental compounds such as e.g. NH<sub>3</sub> and H<sub>2</sub>S.

<sup>&</sup>lt;sup>3</sup> According to the industry, this NO<sub>x</sub> value can be reached under ideal conditions using a fresh new catalyst, but will not be met during normal operation.

A Dual Fuel (DF) engine is not part of the current Protocol. A DF engine in liquid/back-up mode has higher NO<sub>x</sub> emissions than a modern diesel engine due to the lower compression ratio, a DF engine is optimized for natural gas mode operation.

The emission of NO<sub>x</sub> depends on the engine speed. Fuel efficient, large bore, low speed engines tend to have higher NO<sub>x</sub> emissions than faster running smaller engines. When the engine speed is lower, NO<sub>x</sub> concentrations are higher in the combustion chamber because of the longer residence time during which to form NO<sub>x</sub>.

## 7.41.3 Options for reducing emissions from stationary engines

#### Options for reducing emissions to air from liquid fuel-fired (diesel) engines

The main pollutants emitted in the exhaust of a typical (compression ignition) diesel engine burning heavy fuel oil include nitrogen oxides (NO<sub>x</sub>), particulate matter (PM) and sulphur oxides (SO<sub>x</sub>). SO<sub>x</sub> and PM are mainly fuel related emissions. Due to the high efficiency resulting from the high temperature of combustion in stationary diesel engines, emissions of unburned emissions such as carbon monoxide and unburned hydrocarbons are low.

#### Abatement of dust (including PM<sub>10</sub>, PM<sub>2.5</sub> and BC) emissions

When burning heavy fuel oil, dust mainly consists of the ash and sulphur (formed sulphates) contents from the fuel oil and to a smaller extent of soot, BC and hydrocarbons. When burning light fuel oil, the particulate matter mainly consists of soot, BC and hydrocarbons (HCs). BC emissions can be estimated in the range 0.05 to 0.2 g/kg fuel with heavy fuel oil and steady state high load<sup>4</sup>. Secondary cleaning equipment for dust is currently being developed for larger diesel engines<sup>5</sup>. Diesel particulates form under very different conditions of excess oxygen and temperature compared to dust formed in a boiler. The electrical properties (e.g. resistivity, etc.) differ from particulates from a boiler flue-gas, and proper testing of the ESP (electrostatic precipitator) is needed prior to commercial release. The use of engine measures in combination with the use of a low ash and low sulphur fuel, whenever commercially available, can be considered as BAT for reducing dust emissions. Dust concentrations (85 to 100 % of MCR engine load, measurement method ISO 9096 or principally similar other measurement method) lower than 50 mg/Nm<sup>3</sup> at 15 % O<sub>2</sub> (after engine) can be achieved with heavy fuel oil with S concentrations lower than 1.0 wt-%, ash concentration lower than 0.03 to 0.04 wt-%, and asphalthene content lower than 8 wt-%. With heavy fuel oil of lower quality (higher sulphur, ash, and asphalthenes contents) concentrations lower than 75 to 100 mg/Nm<sup>3</sup> at 15 %  $O_2$  can typically be achieved depending on used heavy fuel oil properties. (Remark: Diesel Particulate Filters (DPF) used on heavy duty vehicles and small off road engines are not yet suitable for large stationary diesel engines covered by the guidance document (larger > 5 MWth). Particulate traps are indeed used in many diesel cars and trucks running on clean diesel fuel for filtering off particulates/soot. The trap has to regenerate on a regular basis, i.e. the trapped soot must be burnt out. Precious metal catalysts are often used for regeneration. Oxidation catalysts are sometimes used on clean distillate oil operated diesels equipped with EGR for oxidation of CO, HC and soot. Both systems are based on precious metal catalysts - fast deactivation and clogging would occur with power plant normal fuel qualities. Particulate traps are therefore not yet suitable for large medium/slow speed engines designed to be able to run on heavy fuel oils or other residual fuels. It could be possible for large diesel engines to also run on alternative fuels like LFO).

5 LCP BREF 2006, page 356

<sup>&</sup>lt;sup>4</sup> CIMAC – The International Council on Combustion Engines – Background information on black carbon from large marine and stationary diesel engines – definition, measurement methods, emission factors and abatement techniques -2012

#### Abatement of SO<sub>2</sub> emissions

The sulphur oxide emissions are directly related to the used fuel and to the sulphur content of the fuel. The primary method to reduce the  $SO_x$  emissions is to use a low sulphur content liquid fuel or natural gas if commercially available. Currently few diesel engine systems are equipped with DESOX (desulphurization units) installations and, of these, most are small or medium sized plants and there is little accumulated experience. Here too it should be noted that a diesel flue-gas differs from a boiler flue-gas, for instance it has high oxygen content, which might adversely impact in the performance of the DESOX system. The investment cost for a DESOx plant varies a lot according to the method chosen. The operating cost mainly depends on the amount and type of reagent, water, electricity consumption, and maintenance and waste-product disposal costs. The DESOX system needs proper maintenance in order to work optimally.

#### Abatement of NO<sub>x</sub> emissions

In general, the application of primary methods including the use of better fuel quality to reduce air emissions at source is preferred to secondary measures (end-of-pipe techniques), which is often also costly. During the last decade,  $NO_x$  emissions from liquid fuel-fired diesel engines have been reduced considerably by primary measures as a result of extensive research and development work on the engine, whilst maintaining its high efficiency. Nevertheless  $NO_x$  emissions of diesel engines without secondary measures are still considerable and further reduction needs to be worked on. Primary measures that can be applied for liquid fuel-fired diesel engines, include a base engine optimized for low  $NO_x$ , fuel injection retards, and the addition of water (such as water injection directly into the combustion space, water-in-fuel emulsion, or humidification of the combustion air). If natural gas is available, an option (dependent on engine type, if possible) is to convert of the diesel engine to a low pressure gas dual fuel engine (DF).

The applicable secondary method for diesel engines is the use of SCR (Selective Catalytic Reduction).

#### Control of NO<sub>x</sub> emissions from liquid-fired (diesel) engines

Achievable NO<sub>x</sub> emissions for new heavy fuel oil (HFO) and light fuel oil (LFO) fired stationary medium/low-speed diesel engines with primary dry abatement technique are according to the EU LCP BAT BREF information and according to the new World Bank EHS guidelines 2008 (second generation engines) today below 2000 mg/Nm<sup>3</sup> (15% O<sub>2</sub>). Cost effective and technically suitable primary and secondary exhaust gas cleaning technologies are the focus of today's product development. In general the application of primary methods to reduce air emissions at source is preferred to abatement after formation from the exhaust gas, often at great expense.

Technical measures to reduce  $NO_x$  emissions can be divided into primary and secondary abatement techniques:

<u>Primary methods</u> for liquid fuel-fired diesel engines, such as a base engine optimized for low  $NO_x$  (using the Miller concept - a "dry method"), fuel injection retards, the addition of water (such as water injection directly into the combustion space, water-in-fuel emulsion, or humidification of the combustion air, water emulsion, etc. depending on the application and engine manufacturer). "Dry methods" are preferred in those areas where there is limited access to suitable water supplies. Mechanical, thermal loading and fuel consumption limitation, etc. aspects are factors to consider when applying primary  $NO_x$  reduction methods.

By using a low NO<sub>x</sub> combustion concept in combination with the Miller concept the NO<sub>x</sub> emissions of modern engines is up to 40 % lower than that of a similar engine type from the beginning of 1990s whilst maintaining the same, high, efficiency. The development work is continuing but the turb ocharger is the technical bottleneck; higher pressure ratios are needed in order to enhance the "Miller-concept", otherwise the fuel consumption will increase and power output of the engines might decrease. A new generation of turbochargers is needed if lower NO<sub>x</sub> emissions are to be achieved.

<u>Secondary method</u>: the only applicable secondary method for diesel engines is exhaust gas treatment with SCR (Selective Catalytic Reduction). SCR is an efficient NO<sub>x</sub> abatement technique in cases where it is possible to take into account the following issues related to installation and operation ensuring that the techniques works properly<sup>6</sup>:

- a minimum flue-gas temperature needs to be maintained, depending on the sulphur content of the fuel;
- some trace metals (such as Na, K, Ca, Mg, As, Se, P) might act as catalyst poisons
- if heavy fuel oil or other residual fuels are used, a soot blowing system needs to be installed in the SCR reactor to keep the elements clean and avoid pressure drop increases
- regular maintenance and inspection in order to maintain low ammonia slips that are harmful for components situated after the SCR reactor
- · disposal of used elements
- supply of reagents (pure ammonia, aqueous ammonia or urea) needs to be ensured (infrastructure exists)
- · installation, operation and maintenance costs to be covered

Achievable NO<sub>x</sub> emissions ranges for existing diesel engines with primary measures and secondary measures are described in Table 3 (measurement results from selected references around the world, note ambient relative humidity has a big impact on the resulting NO<sub>x</sub> emissions from a diesel engine). As mentioned above the achievable NO<sub>x</sub> emissions for new diesel engines are now below 2000 mg/Nm<sup>3</sup> in case of primary measures (WB EHS guidelines: 1460 - 1850 mg/Nm<sup>3</sup> at 15 % O<sub>2</sub>), depending on the bore size.

## Table 3: examples of achievable $NO_x$ emissions with emission reduction measures for diesel engines<sup>7</sup>

Diesel engine type	NO <sub>x</sub> emissions (HFO) mg/Nm <sup>3</sup> dry, 15 % O <sub>2</sub>	Remarks
Base engine optimized for low NO <sub>x</sub> (Primary)	2163 – 2178	Standard diesel engine in production, until 2000 (plant in the Caribbean)
Base engine optimized for low NO <sub>x</sub> (primary, second generation)	1739 – 1881	Standard diesel engine in production today (plant in Central America)
Engine with injection retard	Typically up to 10 to 20 % NOx reduction (depends on engine type)	Fuel consumption increase depends on the degree of injection retard, typically up to 3 %
Slow speed engine + 'water addition'	1540	Used mostly in ships, fuel consumption increases, (plant in the Caribbean)
Engine with SCR (Secondary measure)	150 325	diesel oil oil with 0,45 wt-% S

<sup>6</sup> LCP BREF 2006, page 360

<sup>7</sup> LCP BREF 2006, page 379

#### Impacts of fuel quality on the operation of diesel

For diesel engines, fuel quality has a central role on the emissions. The sulphur content of liquid fuels (including HFO and gas oils etc.) alternates /varies typically from 0.1 or less to 4 wt-% S in the UNECE Region Medium sized (up to about 25 MW<sub>e</sub>) and slow-speed engine types (up to about 90 MW<sub>e</sub> unit size) usually operate on more economical fuel oils such as heavy fuel oils, fuel emulsions, refinery vacuum residuals. Small high-speed engines (up to about 5 MW<sub>e</sub> unit size) are operating on distillate oils (low sulphur diesel and ultra low sulphur diesel). Some types of diesel engine can also operate on natural gas and bio-oils.

The fuel quality also has impact on the primary NO<sub>x</sub> abatement methods that can be used. In small high speed applications e.g. EGR (Exhaust Gas Recirculation) and high pressure, electronically controlled injection can be used and lower NO<sub>x</sub> levels achieved compared to the bigger engine types. The "Miller concept" (early closing timing of the air inlet valves, which suppresses the in-cylinder temperatures reducing NO<sub>x</sub> formation) and advanced fuel injection equipment are applicable to bigger modern engine types.

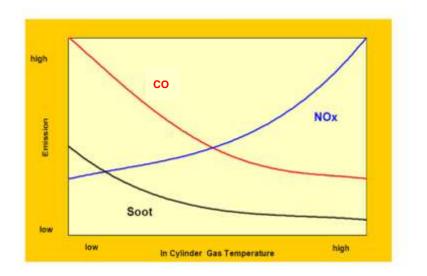
#### Abatement of CO and hydrocarbon emissions from liquid fuelled (diesel) engines

Good engine maintenance is regarded as BAT<sup>8</sup> for the minimization of unburned gaseous air pollutant emissions, a well operated large diesel engine has low CO and hydrocarbon (HC) emissions. CO can be reduced by primary measures aiming at complete combustion. The most important parameter governing the rate of NO<sub>x</sub> formation in a diesel engine is the combustion temperature: the higher the temperature the higher the NO<sub>x</sub> and lower the unburned emissions. There is an optimum balance between the emissions: a lower NO<sub>x</sub> will lead to higher unburned emissions (see Figure 1) and vice versa.

Reducing NO<sub>x</sub> emissions by primary measures may increase other emissions such as CO,  $CO_2$  and particulate matter as shown in Figure 1. Oxidation catalysts may be applied to abate emissions from high speed light fuel oil fired engines but not for engines using heavy fuel oil.

<sup>8</sup> according to the EU LCP BREF document

Figure 1: Typical emission trends for a diesel engine as a function of efficiency (cylinder temperature)



## Control of NO<sub>x</sub> emissions from gas engines, spark-ignited (SG) and dual fuel (DF) (gas mode)

Spark, or otherwise, ignited 4-stroke lean-burn gas engines (SG) are "pure gas" engines, they operate on low pressure natural gas and (depending on engine type) also biogases such as landfill, digester and mine gases. Dual fuel (DF) engines are designed to operate in gas mode on low-pressure natural gas as the main fuel.

By primary engine measures in natural gas mode following NO<sub>x</sub> emissions can be achieved: for leanburn SG engines 95-190 mg/Nm<sup>3</sup> at 15% O<sub>2</sub> and for low pressure gas dual fuel engines 190-380 mg/Nm<sup>3</sup> at 15% O<sub>2</sub>. For other gases than natural gas levels of 95-190 mg/Nm<sup>3</sup> can also be achieved with lean burn SG engines, but possible fluctuations of gas composition and contaminations may have to be considered when defining emission limit values.

The combustion temperature is the most important parameter governing the rate of  $NO_x$  formation in internal combustion engines: the higher the temperature the higher the  $NO_x$  content of the exhaust gases. One method to reduce the combustion temperature is to lower the fuel/air ratio, the same specific heat quantity released by the combustion of the fuel is then used to heat up a larger mass of exhaust gases, resulting in a lower maximum combustion temperature. This primary measure called the lean-burn approach in gas-fired stationary engines is analogous to dry low-NO<sub>x</sub> combustors in gas turbines. Gas fired stationary engine (SG and DF types) installations have low  $NO_x$  levels due to the lean-burn approach.

As the lean-burn engine operates in a leaner mode (enhanced lean-burn) at lower set NO<sub>x</sub> levels with higher specific fuel consumption, the flue gas temperature gets colder and as a consequence the useful heat energy in the flue gas decreases.

In some special applications stationary gas engines are equipped with SCR for additional NO<sub>x</sub> reduction<sup>9</sup>. The driving force for application of SCR is the need to improve local air quality. Strict NO<sub>x</sub>

<sup>&</sup>lt;sup>9</sup> In 2008 in the Netherlands there were about 1000 stationary gas engines using SCR (such as CHP production and CO<sub>2</sub> fertilization in greenhouses). However it should be noted that the feasible investment costs when comparing a power plant to a greenhouse gas application differ considerably."

reduction targets are also needed for some countries with a polluted air-shed in order to meet the obligations of international agreements or EU Directives. In Table 4 achievable  $NO_x$  emission levels for gas fired engines with reduction measures are given.

In some special applications stationary gas engines are equipped with SCR for additional NO<sub>x</sub> reduction. The driving force for application of SCR is the need to improve local air quality. Strict NO<sub>x</sub> reduction targets are also needed for come countries with a polluted air-shed in order to meet the obligations of international agreements or EU directives. For instance, one country has taken action for applying stricter NO<sub>x</sub> ELVs such as 35 mg/Nm<sup>3</sup> for stationary engines with obligation of using SCR, due to the need to take in use all possible reduction measures for different sectors in order to be able to comply with the NO<sub>x</sub> ceiling of the Gothenburg Protocol.

## Table 4: achievable $NO_{\rm x}$ emissions for gas engines (at steady state engine load) according to the EU LCP BREF Document $^{10}$

Engine type	NO <sub>x</sub> emissions, mg/Nm <sup>3</sup> (Dry, 15 % O <sub>2</sub> )	Measure	Remarks
	161-190	Normal rating (primary)	<ul> <li>optimal specific fuel consumption</li> <li>minimum unburned emissions</li> </ul>
	71- 83	Low-NO <sub>x</sub> tuned (primary)	<ul> <li>increase of specific fuel consumption (up to 3% higher) and unburned emissions</li> </ul>
Spark ignited gas engines	5 <sup>11</sup> -19	SCR (secondary)	Driving force for implementation of SCR for gas engines is mainly situations where local air quality standards requests a high reduction of $NO_x$ or ozone emissions, as a result of operation in highly populated areas or the contribution of several industries or mobile sources.
Dual fuel engine - gas mode	144-177		<ul> <li>increase of specific fuel consumption and unburned emissions</li> </ul>
Dual fuel engine - Back-up mode	1531-1751		LFO = light fuel oil (> 0.05 wt-% S)
Gas Diesel - gas mode	1584 – 1612		Natural gas main fuel, pilot fuel heavy fuel oil

#### Unburned emissions from lean burn gas engines

NMVOC emissions from SG and DF engines in gas mode depend on the composition of natural gas. Secondary emission reduction techniques for NMVOC emissions might, in some cases, be needed and an oxidation catalyst for simultaneous CO and NMVOC reduction can be applied. The oxidation catalyst reduction efficiency of NMVOC is very dependent of the hydrocarbon composition in the flue

<sup>11</sup> This NO<sub>x</sub> value can be reached under ideal conditions using a new and fresh catalyst but will not be met during normal operation.

 $<sup>^{10}</sup>$  Tables 7.9 (p.438) and 7.26 (p.466)

gas, especially ethane and propane species are difficult to reduce<sup>12</sup>. CO values kept below 100 mg/Nm<sup>3</sup> (15 %  $O_2$ ) are considered as BAT<sup>13</sup> for gas-fired engine equipped with a new oxidation catalyst.

Based on the information from the engine industry, emission levels around 100 mg/Nm<sup>3</sup>, are only applicable for gas engines (equipped with oxidation catalysts) burning natural gas and not for gas engines burning renewable gases like landfill gas, biogas or purification gas. For them the CO associated level should be at a level of  $110 - 380 \text{ mg/Nm}^3$  (15 % O<sub>2</sub>) in order to represent BAT<sup>14</sup>, due to technical reasons (fuel composition impact).

#### Increase in carbon emissions when decreasing NO<sub>x</sub> emissions

Engine optimization is a compromise between NO<sub>x</sub> emissions, engine efficiency (fuel consumption and thus  $CO_2$  emission) and other emissions (such as CO and hydrocarbons). A reduction in NO<sub>x</sub> emissions by primary measures will increase  $CO_2$  emissions (fuel consumption) as well as "unburned" emissions such as CO, HC, and may also finally lead to misfiring, which might eventually destroy the engine. In operation on biogases, the impurities of the biogas might create deposits on the engine internal components and will thus put restrictions on the achievable NO<sub>x</sub> level. See subheader 9 below (spark ignition engine type). In special cases, such as in polluted urban areas, where SCR is sometimes used to reduce NO<sub>x</sub> emissions the air-fuel ratio can be optimized for best fuel efficiency, and thus also emissions of unburned substances can be reduced. Modern gas engines are knock limited and therefore the potential for operating engines in a richer fuel mode for improved efficiency (and higher NO<sub>x</sub>) and lower CO and HC emissions is limited as other boundary conditions such as engine knock must be respected.

#### Loss of efficiency when decreasing NOx emissions

As the lean-burn engine operates in a leaner mode at lower set NO<sub>x</sub> levels with higher specific fuel consumption, the flue gas temperature gets colder and as a consequence the useful heat energy in the flue gas decreases (detrimental for e.g. steam production in a CHP plant)<sup>15</sup>.

## 7.41.4 Costs of BAT

#### Installation and operation costs of SCR

SCR has a high initial purchase price and, depending on the quality of the fuel used the catalysts will need to be replaced periodically – and used catalyst disposed of in a proper manner. In addition, SCR requires good technical support including spare parts and expertise to operate and maintain. For typical costs of SCR as a function of NO<sub>x</sub> reduction, see Figure 2. Note that the cost and availability of reagent might vary from location to location.

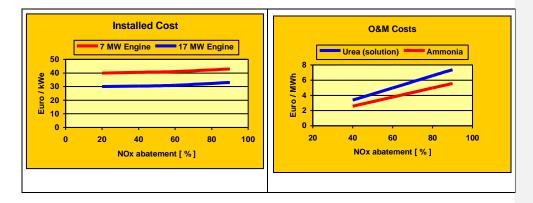
<sup>&</sup>lt;sup>12</sup> Field Experience and Laboratory Analysis of Oxidation Catalyst on Dual Fuel Fuel Engines", by Shazam Williams; Mojghan Naseri; Joe Aleixo; Kristoffer Sandelin, published May, 7, 2006

<sup>&</sup>lt;sup>13</sup> LCP BREF, page 480

<sup>14</sup> subheader 3 in Table 7.36 of LCP BAT BREF

<sup>&</sup>lt;sup>15</sup> Due to deposits formed inside the combustion chamber of biogas (landfill gas, anaerobic fermenter gases) fired engines, NO<sub>x</sub> levels far below 190 mg/Nm<sup>3</sup> at 15% O<sub>2</sub> can not be achieved over the operation life of the engine because of a drift of the emissions caused by isolation effects and change in combustion chamber geometry (Annex 7).

Figure 2: typical costs of SCR as a function of  $NO_x$  reduction rate, heavy fuel oil fired medium speed diesel engine power plant, reagent handling not included. Urea 40% solution 200 euros/ton, aqueous 25% ammonia solution 225 euros/ton)



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Mis en forme : Numéros + Niveau : 1 + Style de numérotation : 1, 2, 3, ... + Commencer à : 1 + Alignement : Gauche + Alignement : 0.63 cm + Retrait : 1.27 cm

**Mis en forme :** Retrait : Gauche : 1.27 cm

Mis en forme : Numéros + Niveau : 1 + Style de numérotation : 1, 2, 3, ... + Commencer à : 1 + Alignement : Gauche + Alignement : 0.63 cm + Retrait : 1.27 cm

**Mis en forme :** Retrait : Gauche : 1.27 cm

Mis en forme : Numéros + Niveau : 1 + Style de numérotation : 1, 2, 3, ... + Commencer à : 1 + Alignement : Gauche + Alignement : 0.63 cm + Retrait : 1.27 cm