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Guidance for the Large Volume Organic Chemicals Sector

Integrated Pollution Prevention and Control (IPPC)







Commissioning Organisation

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Table 0.1: Record of changes

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Executive summary

What is IPPC This Guidance and the	This guidance has been produced by the Environment Agency for England and Wales with the Scottish Environment Protection Agency (SEPA) and the Northern Ireland Environment and Heritage Service (EHS). Together these are referred to as "the Regulator" throughout this document. Its publication follows consultation with industry, government departments and non-governmental organisations. Integrated Pollution Prevention and Control (IPPC) is a regulatory system that employs an integrated approach to control the environmental impacts of certain industrial activities. It involves determining the appropriate controls for industry to protect the environment through a single Permitting process. To gain a Permit, Operators will have to show that they have systematically developed proposals to apply the Best Available Techniques (BAT) and meet certain other requirements, taking account of relevant local factors. This UK Guidance for delivering the PPC (IPPC) Regulations in this sector is based on the BAT
BREF	Reference document BREF (see Ref. 1) produced by the European Commission. The BREF is the result of an exchange of information between member states and industry. The quality, comprehensiveness and usefulness of the BREF is acknowledged. This guidance is designed to complement the BREF and is cross-referenced to it throughout. It takes into account the information contained in the BREF and lays down the indicative standards and expectations in the UK (England and Wales, Scotland and Northern Ireland). The reader is advised to have access to the BREF.
The aims of this Guidance	 The aims of this Guidance are to: provide a clear structure and methodology for Operators to follow to ensure they address all aspects of the PPC Regulations and other relevant Regulations minimise the effort by both Operator and Regulator in the permitting of an installation by expressing the BAT techniques as clear indicative standards improve the consistency of Applications by ensuring that all relevant issues are addressed increase the transparency and consistency of regulation by having a structure in which the Operator's response to each issue, and any departures from the standards, can be seen clearly and which enables Applications to be compared To assist Operators in making applications, separate, horizontal guidance is available on a range of topics such as waste minimisation, monitoring, calculating stack heights and so on. Most of this guidance is available free through the Environment Agency, SEPA or EHS (Northern Ireland) websites
key environmental issues	 (see References). The key environmental issues for this sector are: Fugitive VOC emissions to air - from the numerous storage tanks, flanges, pumps and valves with seals, tanker connections, sample points, and various plant items which are present on large plants. Point source emissions of VOCs to air - from the numerous permitted process release points on these large plants. Waste minimisation - by optimisation of raw material composition and reaction arrangements, and Waste disposal routes - to minimise disposals to landfill. Point source emissions to water - where there are effluent streams containing mixed soluble and insoluble organics, chlorinated hydrocarbons, heavy metals, or non-biodegradable compounds, etc. Odour - where any of the substances produced or used have significant odour potential. Energy efficiency - since many installations are very large users of energy, and the release to air of combustion products often is the biggest single environmental impact by the installation. Noise and vibration - from compressors and other machinery, steam relief valves, large combustion units, flares, etc. Chemical analysis and monitoring of emissions - to improve consistency and comparability of reporting.

• Accident prevention and control - to reduce the occurrence of spillages and other similar environmental accidents.

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1 Introduction

The status and aims of this Guidance

This Guidance has been produced by the Environment Agency for England and Wales, with the Scottish Environment Protection Agency (SEPA) and the Environment and Heritage Service (EHS) in Northern Ireland - each referred to as "the Regulator" in this document. Its publication follows consultation with industry, Government departments and non-governmental organisations.

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It aims to provide Operators and the Regulator's officers with advice on indicative standards of operation and environmental performance relevant to the industrial sector concerned, to assist the former in the preparation of applications for PPC Permits and to assist the latter in the assessment of those Applications (and the setting of a subsequent compliance regime). The use of techniques quoted in the guidance and the setting of emission limit values at the benchmark values quoted in the guidance are not mandatory, except where there are statutory requirements from other legislation. However, the Regulator will carefully consider the relevance and relative importance of the information in the Guidance to the installation concerned when making technical judgments about the installation and when setting Conditions in the Permit, any departures from indicative standards being justified on a site-specific basis.

The Guidance also aims (through linkage with the Application Form or template) to provide a clear structure and methodology for Operators to follow to ensure they address all aspects of the PPC Regulations and other relevant Regulations, that are in force at the time of writing. Also, by expressing the Best Available Techniques (BAT) as clear indicative standards wherever possible, it aims to minimise the effort required to permit an installation (by both Operator and Regulator).

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1.1	Understanding	IPPC
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IPPC and the Regulations	Integrated Pollution Prevention and Control (IPPC) is a regulatory system that employs an integrated
	approach to control the environmental impacts of certain listed industrial activities. It involves determination by the Regulator of the appropriate controls for those industries to protect the environment, through a single permitting process. To gain a Permit, Operators have to demonstrate in their Applications, in a systematic way, that the techniques they are using or are proposing to use, are the Best Available Techniques (BAT) for their installation, and meet certain other requirements, taking account of relevant local factors.
	The essence of BAT is that the techniques selected to protect the environment should achieve an appropriate balance between environmental benefits and the costs incurred by Operators. However, whatever the costs involved, no installation may be permitted where its operation would cause significant pollution.
	IPPC operates under The Pollution Prevention and Control Regulations (for equivalent legislation in Scotland and N Ireland see Appendix 2). The three regional versions of the PPC Regulations implement in the UK the EC Directive on IPPC (96/61/EC). Further information on the application of IPPC/PPC, together with Government policy and advice on the interpretation of the English & Welsh Regulations, can be found in IPPC: A Practical Guide published by the Department for Environment, Food and Rural Affairs (Defra). Equivalent guidance on the Scottish Regulations is provided in PPC Regulations: A Practical Guide (Part A Activities) , published by the Scottish Executive and SEPA. The Department of the Environment, Northern Ireland has published equivalent guidance on the N Ireland Regulations.
Installation based, NOT national emission limits	The BAT approach of IPPC differs from regulatory approaches based on fixed national emission limits (except where General Binding Rules or Standard Permits are issued). The legal instrument that ultimately defines BAT is the Permit, and Permits can only be issued at the installation level.
Indicative BAT Standards	Indicative BAT standards are laid out in national guidance (such as this) and, where relevant, should be applied unless a different standard can be justified for a particular installation. BAT includes the technical components, process control, and management of the installation given in Section 2, and the benchmark levels for emissions identified in Section 3. Departures from those benchmark levels can be justified at the installation level by taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. If any mandatory EU emission limits or conditions are applicable, they must be met, but BAT may go further (see "BAT and EQS" below).
	Some industrial sectors for which national guidance is issued are narrow and tightly defined, whilst other sectors are wide and diffuse. This means that where the guidance covers a wide variety of processes, and individual techniques are not described in detail, the techniques (and their associated emission levels) which might constitute BAT for a particular operation, are more likely to differ, with justification, from the indicative BAT standards than would be the case for a narrow, tightly-defined sector.
BAT and EQS	The BAT approach complements, but differs fundamentally from, regulatory approaches based on Environmental Quality Standards (EQS). Essentially, BAT requires measures to be taken to prevent emissions, and measures that simply reduce emissions are acceptable only where prevention is not practicable. Thus, if it is economically and technically viable to reduce emissions further, or prevent them altogether, then this should be done irrespective of whether or not EQSs are already being met. The BAT approach requires us not to consider the environment as a recipient of pollutants and waste, which can be filled up to a given level, but to do all that is practicable to minimise emissions from industrial activities and their impact. The BAT approach first considers what emission prevention can reasonably be achieved (covered by Sections 2 and 3 of this Guidance) and then checks to ensure that

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			Note IPPC E precautiona an EQS. Conversely, threatened, for expendit	if the appli a more effe	ntal Assess ause the rel cation of inc ective techn I indicative I	sments for ease level a dicative BAT ique is requi 3AT where r	BAT). The BA chieved may l might lead to ired to be BAT	4 of this Guidance and also G AT approach is therefore the m be better than that simply requ a situation in which an EQS is for that installation. The Regu d, ultimately, an installation will	nore lired to mee s still ulations allo
								other related standards and ob nd also in Section 3.	ligations is
Assessing BAT at the sector level			The assessment of indicative BAT takes place at a number of levels. At the European level, the European Commission issues a "BAT reference document" (BREF) for each main IPPC sector. It also issues "horizontal" BREFs for a number of general techniques which are relevant across a series of industrial sectors. The BREFs are the result of an exchange of information between regulators, industry and other interested parties in Member States. Member States should take them into account when determining BAT, but they are allowed flexibility in their application. UK Sector Guidance Notes like this one take account of information contained in relevant BREFs and set out current indicative standards and expectations in the UK. At national level, techniques that are considered to be BAT should represent an appropriate balance of costs and benefits for a typical, well-performing installation in the sector concerned. They should also be affordable without making the sector as a whole uncompetitive, either within Europe or world-wide.						
			The BREF for the Large Volume Organics sector has been published and the indicative standards laid down in this Note are based on the BAT information contained in that BREF, together with information from the other BREFs, where relevant. However, this Note has a wider scope than the BREF of the same name so some indicative standards are based on BATNEEC standards in the IPC Technical Guidance Note for the Large Volume Organic Chemicals sector (see Ref 20).						
Assessing BAT at the installation level			may be just on local fac costs and b Environme Individual ir	ified in eithe tors and, wh enefits of th ntal Asses istallation o	blicability of sectoral indicative BAT standards at the installation level, departu- ther direction. Selection of the technique which is most appropriate may dep where the answer is not self-evident, an installation-specific assessment of t the available options will be needed. The Regulator's guidance IPPC essments for BAT and its associated software tool may help with the assess or company profitability (as opposed to profitability of the relevant sector as to be considered, however.			hay depend lent of the assessmer	
			 that expended decisive factorial decisive factorial decisive factorial different indicative or the Barrow of plant furnace in terms or a num 	iture, are al tors in deci allation's teo from those re BAT stan AT cost/ber is due for re is due for a of local inv nber of expe	lways factor sions about chnical char assumed in dards may r hefit balance enewal/renc rebuild). Ir estment cyc ensive impro	s to be take adopting in acteristics o n the sector not be appro- of an impro- vation (eg. o a effect, thes cles.	n into account dicative BAT v r local environ al assessment opriate: ovement only t change to a di se are cases w	improvements and the timing . However, they should only by where: mental conditions can be show of BAT described in this guida becomes favourable when the fferent design of furnace when here BAT for the sector can be these cases, a phasing progra- ears to be rewarding a poorly p	wn to be so ance, that th relevant ite n the existin e expresse amme may

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Innovation			ndicative BA reasonably a and which fur aims of the P nstallations a he indicative mprovement petter availat opportunities	T standards llows imple rther reduce PC legislati as a part of BAT stand is in techno ble techniqu not foresee General Bind	s criteria, ie mentation in e emissions ion is contir progressive ards at the logy - and the logy - and the les. The ter en in the Gu	techniques n the relevant and their in nuous impro- e sustainable time of writin his Guidanc chnical char uidance, and	which have been deve at sector, which are tech pact on the environme vement in the overall e e development. This S ing but Operators shoul e note cannot be cited acteristics of a particula I as BAT is determined	ative techniques that advance eloped on a scale which chnically and economically viable ent as a whole. One of the main nvironmental performance of ector Guidance Note describes d keep up-to-date with as a reason for not introducing ar installation may also provide at the installation level (except in sider these even where they go
New install	lations	ı i	more difficult	to justify de - and for ne	epartures in ew activities	the case of , techniques	new installations (or new installations (or new installations) or new installations (or new installations) or e	ing installations, but it will be ew activities in existing d indicative BAT requirements
Existing in standards	stallations		standards im achieved. In standard may and otherwis nstallation w environmenta	mediately if such circur y be accept e comply w ill involve a al considera	the cost of nstances, c able, provic ith the requ ssessment ations, but v	doing so is operating tec led that they irements of of the techn where there	disproportionate to the hniques that are not at represent what is con- the Regulations. The c ical characteristics of th s a significant difference	ance with indicative BAT environmental benefit to be t the relevant indicative BAT sidered BAT for that installation determination of BAT for the he installation and local ce between relevant indicative ements on a reasonably short
Existing in upgrading		; \	will be expec	ted to have	upgrading	plans and ti		perators of existing installations scales for upgrading will be set re details.

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1.2 Making an application

A satisfactory Application is made by:

- addressing the issues in Sections 2 and 3 of this guidance;
- assessing the environmental impact described in Section 4 (and in England and Wales Environmental Assessment and Appraisal of BAT (IPPC H1));

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demonstrating that the proposed techniques are BAT for the installation.

In practice, some Applicants have submitted far more information than was needed, yet without addressing the areas that are most important - and this has led to extensive requests for further information. In an attempt to focus application responses to the areas of concern to the Regulator, Application forms (templates) have been produced by the Environment Agency, by SEPA and by EHS in N Ireland. In addition, as the dates for application have approached, the operators in most industrial sectors in England and Wales have been provided with Compact Discs (CDs) which contain all relevant Application Forms, technical and administrative guidance, BREFs and Assessment tools, hyper-linked together for ease of use.

There is such CD for Operators in the Speciality Organic Chemicals sector in England and Wales. The tools and advice on the CD help steer the operator through the Application process, define much more closely the level of detail required in the Application and aim to make the process of calculating impact assessment much simpler.

For Applicants with existing IPC Authorisations or Waste Management Licences, the previous applications may provide much of the information for the PPC application. However, where the submitted Application refers to information supplied with a previous application the Operator will need to send fresh copies - though for many issues where there is a tendency for frequent changes of detail (for example, information about the management systems), it will be more appropriate simply to refer to the information in the Application and keep available for inspection on site, up-to-date versions of the documents.

For further advice see IPPC Part A(1) Installations: Guide for Applicants (for England and Wales) or PPC Part A Installations: Guide for Applicants (for Scotland) or the equivalent Northern Ireland guide for Applicants.

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1.3 Installations covered

The Note covers installations containing activities, described as follows in Part A(1) of Schedule 1 to **The Pollution Prevention and Control Regulations** (for England and Wales). For the equivalent Regulations in Scotland and Northern Ireland see **Appendix 2**

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Installations for the manufacture of organic chemicals in large volume are listed for regulation in Sections 4.1, (a) (i-iv, vi, viii and ix) of Schedule1 to the Regulations. The manufacture of lower volume, speciality organic chemicals included in these and other sub-sections of Section 4.1, and in Sections 4.4, 4.5 and 4.6, is covered by the IPPC Guidance Note on Speciality Organic Chemicals (IPPC S.4.02).

Section 4.1 - Organic Chemicals

Part A(1)

a) Producing organic chemicals such as:

- (i) hydrocarbons (linear or cyclic, saturated or unsaturated, aliphatic or aromatic)
- (ii) organic compounds containing oxygen, such as alcohols, aldehydes, ketones, carboxylic acids, esters, ethers, peroxides, phenols, epoxy resins
- (iii) organic compounds containing sulphur, such as sulphides, mercaptans, sulphonic acids, sulphonates, sulphates and sulphones and sulphur heterocyclics
- (iv) organic compounds containing nitrogen, such as amines, amides, nitrous-, nitro- or azo -compounds, nitrates, nitriles, nitrogen heterocyclics, cyanates, isocyanates, di-isocyanates and di-isocyanate prepolymers
- (vi) organic compounds containing halogens, such as halocarbons, halogenated aromatic compounds and acid halides
- (viii) plastic materials, such as polymers, synthetic fibres and cellulose-based fibres
- (ix) synthetic rubbers

Most LVOC processes are continuous and are often related to a petroleum refinery, from which they may receive raw materials and utilities and may return by-products and wastes. They represent a wide range of different chemical processes with some common features.

This Note is derived in part from the Large Volume Organic Chemicals BREF (Reference 1) whilst focusing on processes operated in the UK, but it also leans heavily on the IPC Technical Guidnace Note of the same name (Reference 20). The BREF includes detailed descriptions of seven illustrative processes as well as descriptions of generic production processes and emission abatement techniques and should be used by applicants for Permits to supplement this Technical Guidance.

Installations, in addition to the main activities, include associated activities which have a technical connection with the main activities and which may have an effect on emissions and pollution. They include, as appropriate:

- raw material storage and preparation
- fuel storage
- chemical reaction and separation
- product handling and storage
- storage and dispatch of finished products
- the control and abatement systems for emissions to all media

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However, the impact of the installation's activities on the wider environment may be more extensive than immediately around the on-site operations. This Note, in line with the requirements of the Regulations, cover issues downstream of the installation such as the final disposal of wastes and wastewaters.

Environment Agency advice on the composition of the installation(s) and which on-site activities are to be included within it (or them) is given in its guidance document IPPC Regulatory Guidance Series No.5 - Interpretation of "Installation" in the PPC Regulations www.environment-agency.gov.uk Operators are advised to discuss the composition of their installations with the Regulator before preparing their Applications.

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1.4 Timescales

1.4.1 Permit review periods

Permits are likely to be reviewed as follows:

- for individual activities not previously subject to regulation under IPC or Waste Management Licensing, a review should be carried out within four years of the issue of the PPC Permit
- for individual activities previously subject to regulation under IPC or Waste Management Licensing, a review should be carried out within six years of the issue of the IPPC Permit

However, where discharges of Groundwater List I or List II substances have been permitted, or where there is disposal of any matter that might lead to an indirect discharge of any Groundwater List I or II substance, a review must be carried out within four years as a requirement of the Groundwater Regulations.

These periods will be kept under review and, if any of the above factors change significantly, they may be shortened or extended.

1.4.2 Upgrading timescales for existing plant

Existing installation timescales

Unless subject to specific conditions elsewhere in the Permit, upgrading timescales will be set in the Improvement Programme of the Permit, having regard to the criteria for improvements in the following two categories:

- 1 Standard "good-practice" requirements, such as, management systems, waste, water and energy audits, bunding, housekeeping measures to prevent fugitive or accidental emissions, good waste-handling facilities, and adequate monitoring equipment. Many of these require relatively modest capital expenditure and so, with studies aimed at improving environmental performance, they should be implemented as soon as possible and generally well within 3 years of issue of the Permit.
- 2 Larger. more capital-intensive improvements, such as major changes to reaction systems or the installation of significant abatement equipment. Ideally, and where there is considerable divergence from indicative BAT standards, these improvements should also be completed within 3 years of Permit issue but longer time-scales may be allowed by the Regulator, where justified in objective terms.

Local environmental impacts may require action to be taken more quickly than the indicative timescales above, and requirements still outstanding from any upgrading programme in a previous permit should be completed to the original time-scale or sooner. On the other hand, where an activity already operates to a standard that is close to an indicative requirement a more extended time-scale may be acceptable. The requirement by the Regulator for capital expenditure on improvements and the rate at which those improvements have to be made, should be proportionate to the divergence of the installation from indicative standards and to the environmental benefits that will be gained - except where there are statutory deadlines for compliance with national or international requirements.

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The Operator should include in the Application a proposed programme in which all identified improvements (and rectification of clear deficiencies) are undertaken at the earliest practicable opportunities. The Regulator will assess BAT for the installation and the improvements that need to be made, compare them with the Operator's proposals, and then set appropriate Improvement Conditions in the Permit

1.5 Key issues

The key environmental issues for the large volume organic chemical manufacturing sector are:

1.5.1 Fugitive emissions to air

The main components of fugitive releases to air from LVOC plants are VOCs. The installations contain large numbers of plant items, flanges, pumps and valves with seals, storage tanks, tanker connections, sample points, etc. and all have the potential for leakage of VOCs. This can occur through relaxation or progressive wear-and-tear of sealing materials, through sloppy operation, maintenance or design, or through failure of equipment. Apart from releases of material through accidental mal-operation or equipment failure, fugitive losses from individual pieces of equipment are usually small - but on a large-scale plant the aggregated total can be very significant.

Section 2.2.4 - Control of fugitive emissions to air - of this Guidance Note covers relevant issues and, in addition, emissions from storage and loading are covered in detail in the LVOC BREF Section 5.3.1.2 and other fugitive emissions in Section 5.3.1.3 (pp 104 - 113)

The basic rules are:

- Operators should aim to minimise fugitive releases of liquid and gaseous organics at the design stage by the specification of high quality items and materials of construction which minimise leakage. The priority is environmental protection rather than cost-effectiveness of the equipment in terms of the financial savings from material that is not lost.
- For on-going fugitive emission prevention, operators should have a formal Leak Detection and Repair (LDAR) programme in place and, where necessary, replace with higher quality item, equipment which continues to generate significant fugitive emissions.

1.5.2 Point source emissions to air

Some plants in the LVOC sector contain large numbers of permitted routine process release points, and they vary in size and throughput from the very small to stacks for the discharge of combustion gases from very large combustion plant.

Gaseous emissions from these sources on most plants have been individually characterised and significantly reduced (in total) since the introduction of the IPC regime across the sector in 1992-1995. However, areas remain where considerable improvement can still be made. For some installations, IPC Improvement Programme conditions are still in the process of being completed - either because they stemmed from 4-year or similar reviews, or because the list of BATNEEC improvements identified as being necessary on some very large installations was large enough to require prioritisation and an longer-term on-going programme of implementation.

The chemical sector as a whole still emits, through point source and fugitive releases, more than a quarter of the total VOCs reported to the Environment Agency's Pollution Inventory (ie. VOCs from all IPC-regulated processes) and LVOC installations are likely to be the major contributors to this total.

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Though the industry is currently reducing its VOC emissions by 12-17% annually, general VOC emission reduction remains a priority for all, and specific VOCs (and a few non-VOC pollutants) a particular priority for some.

Individual sources of air emissions from particular processes are indicated in Section 2.1 - In-process controls - in this Note. Details of potential emissions from many LVOC processes are provided in Chapters 3 and Chapters 7-13 of the LVOC BREF, with BAT abatement techniques for air pollutants and emission levels associated with those BAT techniques described in Section 6.4 (pp 136-140).

1.5.3 Waste minimisation and waste disposal routes

The LVOC sector is diverse and wastes are very process-specific, but some parts of the sector do generate significant quantities of waste. Many installations recover the energy value of wastes where they are combustible but some installations have major disposals of waste to landfill - an activity which, as well as being among the least likely to be recognised as BAT, has become more constrained with the implementation of the Landfill Directive.

Operators should assess their activities against the BAT criteria laid out in Sections 2.4, 2.5 and 2.6 of this Guidance Note.

1.5.4 Emissions to water

Many LVOC installations have relatively small or easily treatable aqueous waste streams but a number have effluent streams containing more complex pollutants such as mixed soluble and insoluble organics, chlorinated hydrocarbons, heavy metals, or non-biodegradable compounds. Where it is not practicable to prevent the generation of these "difficult" waste water streams in the first place, they need to be segregated and treated separately, before being discharged to communal effluent treatment facilities. Effluent streams specific to individual process are identified in Section 2.1 and its subsections in this Note, and treatment techniques are covered in Section 2.2.3. More detail on available techniques is provided in the Waste Water and Waste Gas Treatment BREF.

1.5.5 Odour

Many of the substances produced or used in installations covered by this Note have the odour potential to cause offence to neighbouring communities This is a key issue for some installations, though probably not for the majority in the sector. The issues are covered in more detail in Section 2.2.6 - Odour - in this Guidance Note.

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1.5.6 Energy efficiency

Many LVOC installations are very large users of energy and the release to air of combustion products often has the biggest single environmental impact from the installation. Most installations will be participants to a Climate Change Agreement or a Direct Participant Agreement (which are deemed to satisfy the BAT requirement for energy efficiency) but even at these installations there may be some issues which need to be addressed in the PPC Permitting process. (See Section 2.7 - Energy - in this Guidance Note.)

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1.5.7 Noise and vibration

Noise and vibration are constant features of most LVOC plants - from compressors and other machinery, steam relief valves, large combustion units, flares, etc. Guidance is provided in Section 2.9 - Noise - in this Note and in greater detail in the horizontal guidance note H3 Part 1 - Noise.

1.5.8 Chemical analysis and monitoring of emissions

Emissions monitoring has, to date, been variable within the sector. With national reporting and comparing via databases like the Pollution Inventory, becoming the norm, it is imperative that more consistency is applied to the streams and substances that are monitored and to the methods of analysis used. Further guidance is being developed but interim guidance is provided in Section 2.10 - Monitoring - in this Note.

1.5.9 Accident prevention and control

Over the last few years there have been a number of spillages of organic liquids from plants within the sector that have contaminated land, groundwater or surface water. Whilst major accident hazards and associated environmental risks are likely to be covered by the requirements of the COMAH Regulations there is a need for operators to demonstrate that they have lesser risks well controlled. Section 2.8 - Accidents - in this Guidance Note covers indicative BAT for this area.

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1.6 Summary of emissions

The Large Volume Organics sector is wide and almost any substance might conceivably be a potential release to any medium - so it is considered that there is little value in providing a releases summary of the type used in some other sectoral Guidance Notes.

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1.7 Technical overview

Many different processes are covered by this Note and it is not possible to provide detailed descriptions of them. Instead, brief outline descriptions and flow diagrams are given for the main LVOC processes operated in the UK, together with an indication of their main emissions and any BATs special to the process. Generic BATs common to most of the processes are indicated in Section 2.3.2.

Most LVOC processes are continuous and are often related to a petroleum refinery, from which they may receive raw materials and utilities and may return by-products and wastes. Some processes provide feedstock to downstream processes. They represent a wide range of different chemical processes based on combinations of unit operations. There are, however, several key issues common to most processes such as the control of VOC emissions, the minimisation of wastes and the treatment of waste water.

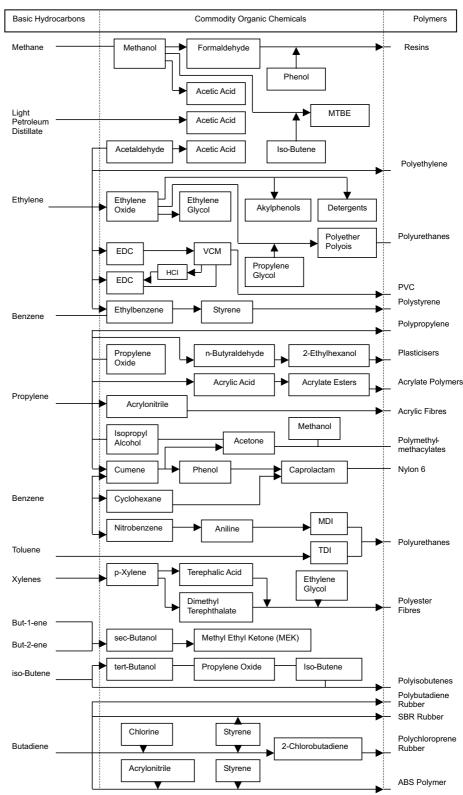
This Note is derived from the Large Volume Organic Chemicals BREF, but focuses on processes operated in the UK. The BREF includes detailed descriptions of a few illustrative processes. In addition to the relevant BATs, there is basic information on aspects of chemical engineering crucial to understanding the technology of the sector, such as unit operations. This detailed information is not repeated here so readers are referred directly to the BREF.

Brief descriptions of the various processes together with their pollution potential are provided in Section 2.1.

An indication of the relationship between the various products and processes is given in **Figure 1.1** below. The process descriptions are set out in the order in which they are listed in the Schedule of activities in the Regulations.

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Figure 1.1: Pathways in the organic chemical industry



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1.8 Economics

The large-volume organic processes are not part of a homogeneous industry. There is a wide range of process types and of plant sizes. While certain abatement techniques are common to many processes, variations in the technical duty can result in very large differences in cost per tonne of product or per tonne of pollution abated. There is also considerable variation in the business background to different production processes, and to the margins achieved. The review in this Note consists of background analysis to assist in the assessment of BAT proposals.

One element in the analysis is the economics and profitability of the relevant industry subsector. The mechanism by which prices are set and the nature of international competition are important factors.

The second element in assessment is that of estimating the abatement costs themselves. Indicative costs of abatement quoted in this Note consist of incremental cash costs plus a capital charge. The incremental cash costs include net variable costs of the abatement measure, and additional fixed costs such as maintenance and taxes. Unless stated otherwise, it is assumed that there is no increase in operating labour and allocated site overheads. The annualised capital charge is calculated using a real discount rate of 10% per year over ten years. This approximates to a typical cost of capital rather than to the opportunity cost to the company. If additional abatement measures are likely to be required in less than ten years, a higher rate of annualisation may be appropriate. Applicants should calculate the costs of abatement in a reasonable and consistent fashion in their applications.

1.8.1 Industry economics

Examples of economic issues specific to the illustrative processes are provided in the BREF in the Sections relating to those illustrative processes.

Background information is given below on two main types of processes: basic LVOCs and commodity polymers, with additional commentary provided on representative other processes.

1.8.1.1 Basic LVOCs

For each process, the number of plants in the UK is typically one to five. Almost all of the plants fall into the category of being large on the criterion of turnover. The operators are large chemical companies or petroleum companies. Many of the plants are relatively old, but most have been periodically revamped in the course of expansions.

Most LVOC processes are based on petroleum feedstocks such as naphtha, gas oil, or associated gas. These petrochemical building blocks such as olefins and BTX aromatics (benzene, toluene and xylenes) are converted in downstream processes to other LVOCs. Final products of the sector include polymer resins for processing into plastic products, solvents and surfactants. The processes reviewed here are typically those in the first or second stage of a processing chain. The products are usually commodity intermediates that are supplied to other chemical plants or companies.

Basic LVOCs are sold on chemical specifications rather than (usually) brand name or performance in use. As a result, competition is focused heavily on price. Within any region, such as Western Europe, different producers have differing costs of production. The differences arise from, for example,

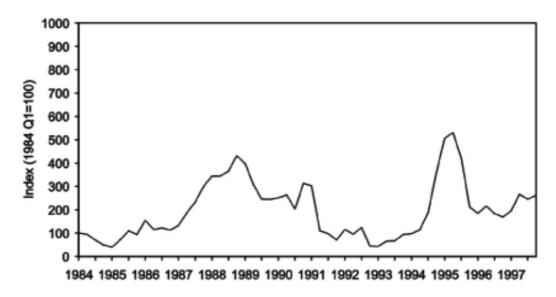
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variations in scale, in feedstock source and type, and in process plant. The price for a product is related to the cost of production of the incremental source of supply, at the more expensive end of the cost curve. In essence, the basic petrochemical business is characterised by competition on price with cost of production playing a very large part.

The commodity LVOC business is highly cyclical. This corresponds to some extent to normal business cycles in demand. It is accentuated by the large-scale nature of the fixed investment, and the understandable tendency for producers to plan new capacity when cash flow is good. With the long lead times of projects, the result frequently leads to over-capacity, temporarily depressing margins.

The cyclical nature of the business is illustrated in Figure 1.2. This is calculated on the basis of cash cost margins for leader plants for a weighted basket of commodity LVOCs and polymers. The leader plant is a model that broadly represents the best 20% of the regional cost curve. For less competitive plants than leaders, the cash cost margin may well be negative in the troughs in the business cycle.





Two further features of this industrial sector are relevant. Firstly, producers may be integrated upstream in preceding processing steps or in refining, or perhaps integrated downstream to final product manufacture. Integration can improve the cost competitive position of companies. Care is therefore needed in assuming that the impact of additional costs will be the same for every company producing a certain basic LVOC. Secondly, competition is on a regional or even a global basis. Regions with low feedstock costs, primarily the Middle East, may produce basic LVOCs and export to Western Europe. For several products, import to the UK is over 50% of UK consumption, whilst other products may show a net export. With this direct competition, it may not be possible to pass on incremental costs to customers.

Cash costs of production are of particular importance in setting prices. This is because capital costs will have been written down in the financial accounts for older plants, and are in any case sunk costs. Cash costs of production for Western European leader plants were typically in the range £150 to £450 per tonne for different LVOCs in 1997. Prices and margins fluctuate with the business cycle. At the peak, most plants generate substantial cash flow, but when a plant is at the less economic end of the regional cost curve, it may suffer negative cash flow in the troughs of the business cycle.

Conclusions of relevance in assessing whether the costs of abatement are excessive are as follows:

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- At some times in the business cycle, companies in the sector generate substantial cash flow while at other times they may suffer a cash shortage or deficit.
- · Special factors such as exchange rate fluctuations can affect profitability.
- It is not meaningful to quote environmental costs as a percentage of margin for a single year; averaging across the business cycle is needed.
- Commodity producers cannot pass on cost increases that apply only to them.
- The position of a plant on the cash cost curve determines whether it breaks even or suffers a significant cash drain in poor times. In practice, this seriously influences companies' decisions on plant closure and exit from the business.

1.8.1.2 Commodity polymers

Commodity polymers include polyolefins, PVC and polystyrene. The polyolefins include low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and variants. Feedstocks to commodity polymer processes are some of the basic LVOCs reviewed above. There are one to five plants for each product in the UK.

The economic dynamics of the commodity polymer business are broadly similar to those for commodity LVOCs. There is a substantial fluctuation in both prices and margins over the industry business cycle. The nature of the market, however, differs in a number of aspects:

- Consumers are plastics processors of varying sizes rather than (usually large) chemical companies; distribution networks and customer service are particularly important.
- Plastic products compete with each other and also with other materials in many applications.
- Polymers must satisfy requirements both for processability and to provide the required attributes of the packaging or other end-product; the product may be supplied compounded in some cases.

Commodity polymers are an increasingly global business, with a move towards large players that focus on certain core business areas. As well as reduced corporate costs, the larger players aim to provide good market coverage and customer support. A number of the major producers in Europe are now joint ventures between companies consolidating a position in specific products.

Western Europe as a whole has been suffering increasing competition from other regions, especially the Middle East with its low-cost hydrocarbon feedstocks. The UK is a large net importer, with imports counting for around half of UK consumption.

With feedstocks priced at market value, the cash costs of production were around £350 to £450 per tonne for the main commodity polymers for Western European leader plants in 1997. The cash cost margin, which takes no account of depreciation or return on capital, has varied over the last decade from negative values to positive margins of over £200 per tonne for Western European leader plants.

The conclusions are the same as those quoted for basic LVOCs.

1.8.1.3 Other processes

The majority of the processes are influenced to some extent by the LVOC business cycle. However, the economic characteristics are increasingly modified when:

A process is several steps downstream from basic hydrocarbon feedstocks. This attenuates the
effects of the LVOC cycle; and

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Strong technical support and customised applications are a very important part of the business. This
tends to move pricing from a commodity cost-plus basis to the more performance-oriented area of
specialities.

1.8.2 Costs of pollution abatement

Some estimates of costs of abatement by different techniques, obtained for the preparation of the IPC Guidance Note for LVOCs (Reference 20) in 1998 are summarised below for illustrative purposes. They are very sensitive to site-specific factors, and the relative cost-ranking of different options may change with the process duty - and, in all cases, the onus is on the operator to demonstrate that cost estimates corresponding to its specific process options are realistic and robust.

1.8.2.1 VOCs from tanks and transfers

Control of evaporative losses from tanks and in loading operations is a common requirement. The cost data given in **Table 1.1** are based on liquid with a vapour pressure of 40 kPa at operating conditions, storage in two tanks of 5,000 m³ each, and transfer of 100,000 tonnes per year. Four road tankers are included in this scope. A nominal credit of £150 per tonne is given for saved VOC.

Abatement technique	Capital cost (£000)	Annualised cost (£)	Cost per tonne VOC (£/tonne)
External floating roof: secondary seal	28	4140	650
Internal floating roof	79	12300	965
Road tanker mods	80	11700	835
Single-stage VRU	710	137650	2900
Plus second-stage VRU (incremental)	115	22700	9550

1.8.2.2 VOCs from continuous vents

There are many techniques for the destruction or recovery of VOCs in continuous vents. The economic data presented in Table 1.2 relate to incineration or recovery by carbon adsorption of around 2000 mg/m^3 of oxygenated organic in a stream of 25,000 m³/hour.

Table 1.2: Cost of Incineration	or Absorption of VOC
---------------------------------	----------------------

Abatement technique	Capital cost (£000)	Annualised cost (£000)	Cost per tonne VOC (£/tonne)
Thermal incinerator - no recuperation	490	456	1170
Thermal incinerator - 70% recuperation	586	238	610
Thermal regenerative	720	176	450

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Table 1.2: Cost of Incineration or Absorption of VOC

Abatement technique	Capital cost (£000)	Annualised cost (£000)	Cost per tonne VOC (£/tonne)
Catalytic incineration	630	201	510
Adsorption	1456	315 (a)	800 (a)

No credit included for recovered VOC.

As well as site-specific factors such as plant layout, the flowrate and VOC concentration affect the economics dramatically. **Table 1.3** illustrates this.

Abatement technique	VOC (mg/m ³)	Flow (m ³)hour)	Annualised cost (£000)
Thermal incinerator - 70% recuperation	2000	25000	238
Thermal incinerator - 70% recuperation	10000	5000	50
Adsorption	2000	25000	315
Adsorption	10000	5000	75

1.8.2.3 Fugitive emission of VOCs

Fugitive emissions of VOCs, occurring as leaks from equipment and fittings, may be tackled in two main ways. For the first selection of high-integrity equipment and fittings it is difficult to split out the true incremental costs. The second approach is to improve maintenance with a leak detection and repair (LDAR) programme.

A simple LDAR scheme, involving annual inspection of gas and volatile liquid service components, is estimated to result in a net annualised cost of £12,000 per year or £760 per tonne VOC. This is for a typical plant handling 20,000 tonnes per year of gaseous hydrocarbon streams and 30,000 tonnes per year of volatile liquids.

1.8.2.4 Control of SO₂ emissions from combustion

Large combustion activities form part of many LVOC processes. If SO_2 arises from the combustion activity, fuel switching is an obvious potential solution. The cost of a fuel switch from high-sulphur fuel oil would be around £300 to £500 per tonne of SO_2 saved, excluding costs of converting burners.

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		Making an application	Installations covered	Timescales	Key issues	Summary of releases	Technical overview	Economics	

1.8.2.5 Control of NO_X emissions from combustion

Low NO_X burners or other combustion modifications are generally accepted as good practice and the incremental cost on new plant is small. An indicative cost is given in **Table 1.4** for a retrofit on an existing plant. Flue gas treatment techniques are more costly but, with other measures, could be considered BAT. The cost estimates in **Table 1.4** are for Selective Non-Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR) on the flue gas from a 40 MW fired heater.

Table 1.4: Cost of NO_X abatement

Abatement technique	Capital Cost (£000)	Annualised cost (£000)	Cost per tonne NOx (£/tonne)
Low NO _X Burners	190	38	1200
SNCR	540	171	3600
SCR	1865	417	6950

1.8.2.6 Water treatment

Aqueous effluent from LVOC activities often passes to a site waste-water treatment plant, but incremental costs arising from the subject processes are difficult to identify. As illustration of alternative (or additional) techniques, the costs of treatment of effluent with a high organic content are shown in **Table 1.5**. The flow is 5 m³/h with an organics content of 5000 mg/l.

Technique	Capital Cost (£000)	Annual Cost (£000 per annum)	Annualised cost (£000 per annum)	Unit Cost £,/m ³)
Incineration	4000	1750	2400	60
Wet air oxidation	5000	360	1170	29
Supercritical water oxidation	7000	690	1830	46

1.8.3 Impact on costs of production

It can be difficult to assess the costs of abatement on a group of processes, or even on one process, because the requirements and the costs will be site-specific - but to put some of the control techniques into an economic context, a simple generic case can be used. It does not represent a specific process,

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but has several elements that occur in a variety of petrochemical facilities. The generic case is shown in **Table 1.6**. (but the process duties for each abatement technique, and the costs of control, are not necessarily the same as those used for illustration in **Table 1.4**.)

Table 1.6: Generic petrochemical plant

Element	Unit	Basis
Production (liquid of moderate volatility)	tonne per year	200000
Feedstock (liquid at ambient conditions)	tonne per year	100000
Purge stream with air	m ³ /h	50000
	g/m ³	5
Difficult aqueous stream with organics	m ³ /h	5
Main fired heater/furnace	MW	35

The illustrative abatement techniques are as follows.

For control of losses from storage and loading, three types of techniques are considered. One is the installation of an internal floating roof on the four storage tanks. A single- stage vapour recovery unit (VRU) and a second VRU stage are the other two techniques.

Fugitive losses are taken to be controlled by leak detection and repair (LDAR). Two levels are examined. Level I requires annual inspection of gas and liquid components, while Level II is more stringent. A hydrocarbon purge in an air or inerts stream is assumed to arise from the generic process, though in practice, this is not characteristic of most petrochemical plants, where inerts volumes are usually small. It is possible that streams with a significant organic content could find a home in the site boiler or other heaters, unless there are technical or regulatory problems with this. For the purposes of economic analysis, the abatement technique considered is that of thermal oxidation with energy recovery.

Application of selective catalytic reduction (SCR) to abate NO_X emissions from a process furnace has not been a usual requirement, although regulators elsewhere in Europe have requested it when considering a new ethylene cracker application.

Some processes produce small volumes of difficult aqueous wastes with a significant organic content, such as from caustic scrubbing. The technique considered to abate this is wet air oxidation.

Finally, a nominal cost is included for coating the floors of storage tank bunds with concrete that is impermeable to hydrocarbons, as an example of ground protection measures.

All these are add-on techniques rather than representing any form of fundamental redesign. It is impossible to generalise on the costs of waste minimisation and recycling.

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The costs of the selected abatement techniques on the generic petrochemical plant are shown in **Table 1.7**.

Technique	Capital £000	Annualised cost £000 pa	Cost/tonne of VOC £	Cost/tonne of product £
VOC Internal floating roof	157	25	964	0.12
Loading VRU	1000	190	2000	0.95
Loading VRU (2nd stage: incremental cost)	160	31	6715	0.16
Fugitives level I	40	7	95	0.03
Fugitives level I (incremental cost)	100	53	4400	0.27
Thermox on purge	875	784	400	3.92
OtherSCR	1870	418		2.09
Wet air oxidation	5000	1170		5.86
Ground protection	50	3		0.01

1.8.4 Economic implications of pollution control costs

Fixed capital investment typically ranges between 1 and 6% of gross revenues, and operating profits vary widely over the business cycle, with a typical range of -5% (negative) to +15% (positive) of gross revenue.

The heterogeneous nature of the sector and the cyclical fluctuation in prices and margins make it difficult to suggest definitive cut-off points for acceptability of abatement costs for the sector as a whole. The requirement for regular Environmental Performance benchmarking as outlined in Section 2.1.7, will prioritise the areas for improvement for each installation and inform judgment about the levels of expenditure per tonne of pollutant removed that will be required.

Emissions

controls

Management

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2 Techniques for pollution control

To assist Operators and the Regulator's officers in respectively making and determining applications for PPC Permits, this section summarises the indicative BAT requirements (i.e. what is considered to represent BAT for a reasonably efficiently operating installation in the sector). The indicative BAT requirements may not always be absolutely relevant or applicable to an individual installation, when taking into account site-specific factors, but will always provide a benchmark against which individual Applications can be assessed.

Summarised indicative BAT requirements are shown in the "BAT boxes", the heading of each BAT box indicating which BAT issues are being addressed. In addition, the sections immediately prior to the BAT boxes cover the background and detail on which those summary requirements have been based. Together these reflect the requirements for information laid down in the Regulations.

Although referred to as indicative BAT requirements, they also cover the other requirements of the PPC Regulations and those of other Regulations such as the Waste Management Licensing Regulations (see Appendix 2 for equivalent legislation in Scotland and Northern Ireland) and the Groundwater Regulations, insofar as they are relevant to PPC permitting.

For further information on the status of indicative BAT requirements, see Section 1.1 of this guidance or **Guidance for applicants**.

It is intended that all of the requirements identified in the BAT sections, both the explicit ones in the BAT boxes and the less explicit ones in the descriptive sections, should be considered and addressed by the Operator in the Application. Where particular indicative standards are not relevant to the installation in question, a brief explanation should be given and alternative proposals provided. Where the required information is not available, the reason should be discussed with the Regulator before the Application is finalised. Where information is missing from the Application, the Regulator may, by formal notice, require its provision before the Application is determined.

When making an Application, the Operator should address the indicative BAT requirements in this Guidance Note, but also use the Note to provide evidence that the following basic principles of PPC have been addressed:

- The possibility of preventing the release of harmful substances by changing materials or processes (see Section 2.2.1), preventing releases of water altogether (see Section 2.2.1), and preventing waste emissions by reuse or recovery, have all been considered, and
- Where prevention is not practicable, that emissions that may cause harm have been reduced and no significant pollution will result.

This approach should assist Applicants to meet the requirements of the Regulations to describe in the Applications techniques and measures to prevent and reduce waste arisings and emissions of substances and heat - including during periods of start-up or shut-down, momentary stoppage, leakage or malfunction.

l	Introduction			Techniques for pollution control			Emissions			Impact		
	In-process controls Emissions controls Management		Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring		Installation issues

2.1 In-process controls

This section outlines briefly some of the processes in the Large Volume Organic Chemicals Sector, and indicates the potential waste streams emanating from each. Control of those emissions and waste streams is described in Section 2.2.

2.1.1 Environmental Performance Indicators

Benchmark values in this guidance are typically presented as concentrations (e.g. mg/l, mg/Nm³). Concentrations are the traditional basis for setting emission limits in permits as they are good indicators of unit operation performance but they have limitations. Thus, for England and Wales, the Environment Agency is developing complementary "Environmental Performance Indicators" that could help to target regulatory effort on the most important environmental issues.

Environmental Performance Indicators involve using emission data to:

- Normalise for the scale of process operation to benchmark the emissions from installations that have different sizes and product mixes (e.g. quantity of emitted pollutant per unit of production).
- Calculate "Environmental Burdens" using equivalency factors to determine the significance of emissions in terms of recognised environmental impacts.

Consideration is being given to a range of Environmental Performance Indicators, including:

For Air:

Stratospheric Ozone Depletion,

Global Warming (both from the installation and from imported power),

Photochemical Ozone Creation,

Airborne Acidification.

For Water:

Acidification,

Oxygen Demand,.

Eutrophication.

For Waste:

Waste Hazard Score (from H1),

Waste Disposal Score (from H1).

For raw materials:

Water use (potable and non-potable).

For hazardous substances:

Environmental Health,

Human Health.

Raw

materials

Techniques for pollution control Waste handling

Waste

disposal

Emissions Energy recoverv or

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In the absence of any guidelines for the calculation of Environmental Performance Indicators, there are no indicative BAT requirements. However, operators in England or Wales should demonstrate to the Environment Agency that they have their own methods of monitoring and benchmarking their environmental performance and show how these are used to drive environmental improvements.

Accidents

The choice of Environmental Performance Indicators is left to operators but it should recognise the issues that are listed above. The H1 database tool is advocated as providing a simple solution.

In future the Environment Agency may recommend specific methodologies for calculating Environmental Burden and/or normalising for scale. Research projects are currently under way to develop these systems.

2.1.2 Hydrocarbons

2.1.2.1 Ethylene/propylene

A detailed description of this process is given in the LVOC BREF Chapter 7.

Ethylene is produced by the steam pyrolysis of a gaseous or liquid hydrocarbon feedstock (eg. ethane, naphtha or gasoil). Mixed co-products are also produced including higher alkenes (olefins) such as, butadiene and pentenes. Some reforming can also occur, providing an aromatic rich co-product stream, commonly known as pyrolysis gasoline. The quantity of by-products produced increases as the feedstock molecular weight increases. For example, cracking ethane will produce virtually no coproducts whilst cracking naphtha will yield a broad range of co-products, including propylene.

Feedstock and steam are subjected to high temperature catalytic cracking in a tubular furnace and the resultant gas is cooled in steam-generating facilities and may be oil-guenched. Further cooling in the pyrolysis fractionator results in fuel oil and some gasoline components separating from the main gas stream. The remaining gases are cooled, compressed, and subjected to acid gas removal and dried prior to cryogenic demethanisation. A methane-rich fuel gas stream and an ethylene-ethane fraction are recovered. The latter is further fractionated to produce polymer grade ethylene as well as ethane, which is recycled. Propylene and heavier components are separated by fractionation.

Ethylene crackers tend to be very large plants, processing small molecules at moderate pressure, hence fugitive emissions of feedstocks and products can be significant. Start up and shutdown of the process places heavy demands on environmental systems, particularly the flare.

Potential emissions to air:

- Oxides of carbon and oxides of nitrogen from furnaces, waste gas incinerators, regeneration heaters and acetylene reactor regeneration.
- Hydrocarbons from flares, (start-up, shut-down and process upsets)
- Fugitive emissions.
- Particulates and combustion products resulting from decoking operations.

Special control techniques include:

- Optimisation of furnace design to minimise coking.
- High integrity equipment and fittings on gas and volatile liquid duties.
- Fugitive emission reduction scheme
- Good operating procedures to minimise flaring at startup and shutdown.

Potential emissions to water:

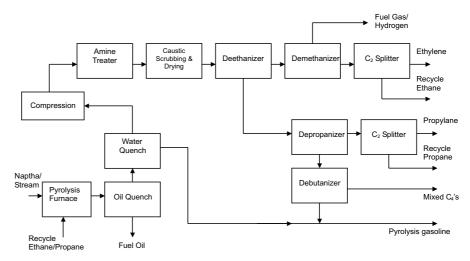
Introduction	Techniques for	echniques for pollution control			Emissions			Impact		
In-process controls Emissions controls Managemen	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

- Polymer from sludge dewatering.
- Zinc/chromium and zinc/phosphorus formulations, hypochlorite and sulphuric acid from cooling tower blowdown.
- · Process condensate from a drying process and spent caustic from acid gas removal.
- Soluble hydrocarbon oils from process purges.

Potential solid waste streams:

- Butadiene polymers from depropaniser waste.
- · Ash and heavy hydrocarbons from oil/water separator sludge.
- · Spent catalyst from the reactor.

Figure 2.1: Ethylene/propylene process: steam cracking of naphtha



2.1.2.2 Butadiene

In Western Europe butadiene is manufactured primarily from the C4 stream produced in the cracking operations for ethylene manufacture. The feedstock is a mixture of hydrocarbons, including butadiene, of similar boiling points. Conventional distillation techniques provide insufficient purification and a solvent extraction or extractive distillation process is used in all three main manufacturing variants. Solvents used include aqueous cuprous ammonium acetate (the CAA process) acetonitrile (the ACN process) and N-methyl pyrrolidone (the NMP process). Each process with its waste streams is described in turn. Additional information is provided in Chapter 7 of the LVOC BREF (pp 143-194)

The Cuprous Ammonuim Acetate (CAA) process

Mixed C4 hydrocarbons are extracted counter-currently with a 20% CAA solution in a series of mixer settlers. Distillation of the rich CAA solution at successively increasing temperature liberates the lower boiling hydrocarbons first and, at 80°C, butadiene, which is purified by redistillation. Polymer buildup in the circulating solvent (which would otherwise cause process problems due to fouling) is reduced by passing it through carbon absorbers. The C4 feed is pre-treated to remove acetylene which would otherwise complexes.

Potential emissions to air

· Hydrocarbons and ammonia from distillation and storage tank vents.

Potential emissions to water

Copper compounds, ammonia and hydrocarbons as process and solvent wastes to water.

Introduction			Techniques for pollution control			Emissions			Impact		
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

Potential solid waste streams

Copper-containing sludges, charcoal and polymerised hydrocarbons will be disposed of as solid waste.

The Acetonitrile (ACN) process

The ACN process comprises feed preparation, extraction, purification and solvent purification and recovery. Oxygen can initiate unwanted polymerisation and is removed from the feedstock by washing with sodium nitrite solution. Washed hydrocarbons are then distilled to remove C3 hydrocarbons. The vapour phase mixed hydrocarbons are contacted and absorbed in acetonitrile; butanes and butene remaining largely unabsorbed. ACN, rich in butadiene, is distilled and butadiene removed with some butenes, acetylenes and 1,2-butadiene. Further distillation gives the purified product. Impurities gradually build up due to the degradation of the ACN solvent. They are removed by taking a bleed from the circulating solvent and diluting it with water. Any polymers separate as an oil in a coalescer. Acetamide and ammonia are removed in a solvent recovery column by distillation. Recovered ACN is recycled.

Potential emissions to air

 Acetonitrile, hydrocarbons and ammonia will be released from reactor vents, solvent recovery column vents and during plant decommissioning for maintenance. Acetamide will be released from solvent recovery column vents.

Potential emissions to water

 Ammonia and acetamide will be discharged with solvent recovery waste waters, and acetonitrile in process waste waters. Sodium nitrite and sodium nitrate are released in deoxygenation waste waters.

Potential solid waste streams

Polymers will form a solid waste from the distillation process.

The N-methyl pyrrolidone (NMP) process

In the NMP process, counter-current extraction of the feedstock produces a pure butenes stream and a pure butadiene stream. The solvent is regenerated on a continuous basis in vacuum evaporation vessels to remove polymeric solids. Acetylenes and C5 hydrocarbons are removed by distillation, with sodium nitrite added as a scavenger to inhibit polymer formation.

Potential emissions to air

 Hydrocarbons lost from reactor and storage tank vents and during process plant decommissioning for maintenance.

Potential emissions to water

N-methyl pyrrolidone and sodium nitrite are lost to water in process purges.

Potential solid waste streams

 Residue sludge formed from the regeneration of spent N-methyl pyrrolidone which contains NMP, NMP polymers, sodium nitrate and butadiene.

2.1.2.3 Acetylene

There are a number of processes for the manufacture of acetylene. These include:

- from hydrocarbons pyrolysis, natural gas oxidation, electric arc
- from calcium carbide dry hydrolysis, wet hydrolysis

Introduction	Techniques for pollution control			Emissions			Impact			
In-process controls Emissions Ma	anagement		Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

Acetylene is used in the UK primarily as a fuel gas and not as a chemical intermediate. It requires a production process which can be stopped and started according to market demand. In the UK, all acetylene is produced by the chemical reaction between calcium carbide and excess water in a generator. The manufacturing process can be subdivided into the following stages

- calcium carbide handling
- gas generation
- purification
- collection and processing of lime
- charging of cylinders

Calcium carbide is fed into the generator and water added for both reaction and cooling purposes

A by-product of the reaction is calcium hydroxide (lime) which is removed from the generator to settling tanks or pits. The acetylene leaving the generator is contaminated with the hydrides of the impurities which were present in the carbide. After ammonia scrubbing and removal of hydrogen sulphide and phosphine, the acetylene is passed through a drier. Calcium chloride or molecular sieve may be used as a drying medium. Currently, calcium chloride is used in the UK.

The acetylene is compressed and charged into cylinders under pressure, where it is dissolved into acetone contained in a porous media (mass). Typically acetone storage tanks are blanketed with nitrogen.

Potential emissions to air:

- Acetylene, ammonia, hydrogen sulphide and phosphine from purging of the generator feed hopper.
- Acetylene from the purification bed vent during regeneration.
- Ammonia and hydrogen sulphide from lime pits.

Potential emissions to water:

- Glycol from raw gas holding tank condensates contributing to BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) wastewater loadings).
- · Condensed water vapour from acetylene cooling combining with the gas holder glycol water seal.
- Oil from compressors.
- Calcium chloride from drier blowdown.
- Potential solid waste streams.
- Ammonia and hydrogen sulphide from the ammonia scrubber used to purify raw acetylene.

Potential solid waste streams:

- Carbon and ferrosilicates from the generator (the result of unreacted impurities in the carbide).
- Chromium and mercury from spent purifier bed solids.

2.1.2.4 Cumene

Cumene is produced from a reaction between propylene and benzene. The propylene feedstock contains propane as an inert impurity. The reaction is carried out under pressure at 250°C and catalysed by phosphoric acid on kieselguhr. Excess benzene is used to ensure complete conversion of the propylene. Products are separated by distillation, where propane is removed. Higher alkylated benzene by-products may be converted to cumene by transalkylation with additional benzene. Unreacted benzene is recycled to the reactor.

Potential emissions to air:

- Storage tank blanket gases containing hydrocarbons.
- Oxides of carbon from purge and let down gases routed to flare.

Introduction		Techniques for p	collution control		Emissions			Impact			
In-process controls		Raw materials	handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

Potential emissions to water:

Phosphoric acid, hydrocarbons and amines from acid pot drainings and decommissioning washes.

Potential solid waste streams:

• Spent catalyst and process residues.

2.1.2.5 Ethylbenzene

Ethylbenzene is produced in the in the UK by the vapour phase alkylation of benzene with ethylene over a proprietary zeolite catalyst. Both reactants are pre-dried. The product is isolated by successive distillation stages to remove benzene, which is recycled to the feed, and polyethylbenzene which is returned to the reactor. Impurities such as methane, hydrogen and ethane are separated from the reactor products and routed to the refinery fuel gas system. Pre-drying is by molecular sieves which are regenerated using process gas at 220°C. The zeolite catalyst is regenerated by burnoff using recirculated nitrogen containing 0.6 to 0.7% oxygen. A bleed of gas is vented to atmosphere to remove the resultant carbon dioxide.

An alternative liquid-phase alkylation process is described in the VOC BREF, Chapter 3.3 (p.31).

Potential emissions to air:

- Oxides of carbon and oxides of nitrogen from catalyst regeneration.
- Losses of benzene and other compounds from tank vents and loading operations
- Fugitive losses of ethylene, benzene, ethylbenzene from equipment and fittings

Potential emissions to water:

Benzene in the dehydration water and hydrocarbons in steam condensate.

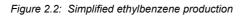
Potential solid waste streams:

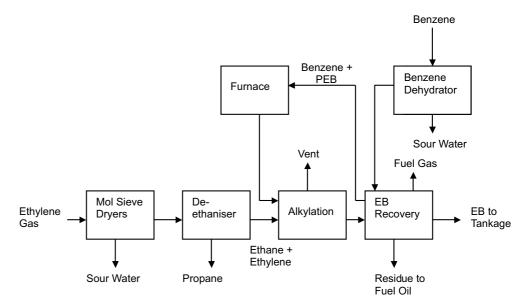
Spent molecular sieve material.

Special control techniques include:

- Double mechanical seals on pumps
- Containment of benzene vapours from tanks
- Loading and stripping of organics from wastewater

Introduction	1		Techniques for	pollution control		Emissions			Impact			
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring		Installation issues	





2.1.2.6 Styrene

The majority of styrene is manufactured in a two-stage process comprising the catalytic alkylation of benzene with ethylene to produce ethylbenzene (EB), followed by the catalytic dehydrogenation of EB to produce styrene. Ethylbenzene production is discussed in Section 2.1.1.5.

Styrene can also be produced as a co-product via an air oxidation route. This process is not currently used in the UK and is not described further.

A number of different routes exist for the manufacture of styrene monomer, but currently the only two commercially-utilised routes are dehydrogenation of EB and air oxidation of EB. This second process consists of oxidation of EB to ethylbenzene hydroperoxide, followed by reaction with propylene to give alphaphenyl ethanol and propylene oxide; the alcohol being then dehydrated to styrene. In the UK, styrene is currently produced solely by the catalytic dehydrogenation of EB as described below.

Purified EB is vaporised, mixed with superheated steam, and fed to the dehydrogenation reactor. The catalysts are generally formulated on an iron oxide base including chromium and potassium. Reaction products are condensed and separate into two phases, water and crude styrene. Hydrogen-rich process gas is recovered and used as fuel in the steam superheater and process water is normally purified in a stripper and recycled to the boiler. Crude liquid styrene, consisting primarily of styrene and EB with traces of toluene, benzene, and tars, is transferred to storage.

Crude styrene is purified using low temperature vacuum distillation in conjunction with sulphur or nitrogen-based inhibitors to minimise polymerisation of vinyl-aromatic compounds. This process recovers benzene, EB, and toluene. Toluene is normally sold, benzene returned to the EB alkylation reactor and EB recycled to the reactor feed. Tars are removed as distillation column residues. Purified styrene is mixed with inhibitor and transferred to storage tanks. In some facilities, an EB/benzene/ toluene stream is separated from the crude styrene initially and processed separately.

Potential emissions to air:

- Benzene, toluene, EB, styrene.
- Hydrogen from catalyst preparation.
- Benzene, EB from distillation processes.

Introduction		Techniques for	pollution control		Emissions			Impact			
In-process controls Emission controls	ns Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

- Styrene monomer from storage tanks.
- EB, benzene, toluene and styrene emissions from the purification process.

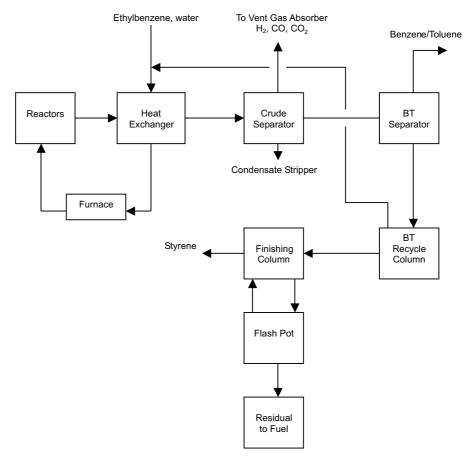
Potential emissions to water:

• Steam condensate containing EB, benzene, toluene and styrene.

Potential solid waste streams:

- Residue from distillation columns.
- Sulphur or nitrogen-based residues from styrene purification.
- Spent catalyst.

Figure 2.3: Manufacture of styrene: ethylbenzene dehydrogenation



2.1.2.7 Higher Olefins

Higher olefins are linear olefins (alpha and internal) in the carbon range C6 to C20. The product from the higher olefin process depends on both the process technology and the feedstock. Ethylene and propylene/butene feedstocks are used in the U.K. The process consists of two complementary techniques:

- Oligomerisation for synthesis of alpha olefins from ethylene.
- Isomerisation/disproportionation for conversion of light and heavy alpha olefins to internal olefins.

Oligomerisation is catalysed by a metal ligand catalyst dissolved in a solvent that is largely immiscible with the alpha olefin product. A three phase mixture - solvent containing catalyst, oligomer product and ethylene gas - is circulated through a series of reactors. The heat of reaction is removed by water-

Management

Noise

Installation issues

Closure

cooled exchangers. As product is formed it separates from the solvent-catalyst phase and enters the hydrocarbon phase. The product is separated from the catalyst solution and ethylene which are recycled; the product is scrubbed with solvent to remove catalyst.

Accidents

Dissolved ethylene in the product is recovered by distillation for recycle. The product is then distilled to recover individual olefins and by-products which are fed to the second reaction stage of isomerisation/ disproportionation. The reactors are operated at 80-120°C and 68-136 barg. Reaction rate is controlled by the rate of catalyst addition.

Ethylene is converted to a range of alpha olefins of even carbon number by an oligomerisation reaction.

In the second process step light C4 olefins and C20+ olefins (plus unwanted C6 - C18 olefins) are converted to mid-range C6 - C14 internal olefins by molecular rearrangement. The double-bond is shifted away from the alpha position to any of the internal positions.

Isomerisation/disproportionation is carried out at 80-140°C and 4-17 barg, with negligible heat generation. Feedstocks are first purified to remove alpha olefins, catalyst and solvent residues. Double bond isomerisation of the alpha olefins and disproportionation are controlled by separate catalyst systems. The desired products are separated from the resulting reaction mixture by distillation and unwanted fractions are recycled. Impurities are removed in process bleed streams.

Potential emissions to air:

- Oxides of carbon and oxides of nitrogen from on-site incinerators.
- Hydrocarbons from storage tank vents and the incineration of tank bottoms.
- Nickel from incineration of interceptor sludge and catalyst.

Potential emissions to water:

Nickel compounds from aqueous interceptor discharge.

Potential solid waste streams:

Cobalt and molybdenum from spent catalyst.

2.1.3 Organic compounds containing oxygen

2.1.3.1 Ethanol

Most industrial ethanol is manufactured by the vapour phase hydration of ethylene over a solid catalyst. Ethylene and water vapour are passed over a phosphoric acid catalyst supported on porous clay beads at around 240°C and 68 barg. The reactor product is scrubbed with water to separate the ethanol. Unreacted ethylene is recycled. Ethanol is obtained from its aqueous solution by a series of distillations, followed by azeotropic distillation with benzene.

Potential emissions to air:

Hydrocarbons from process vents.

Potential emissions to water:

Caustic effluent from washing of the aqueous product prior to distillation and phosphates from the distillation process.

Potential solid waste streams:

Organic solvents, phosphoric acid and phosphates from spent catalyst.

Introduct	on		Techniques for	pollution control		Emissions			Impact		
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

2.1.3.2 Isopropanol

There are two distinct methods for manufacturing isopropyl alcohol:

- Indirect hydration of propylene using sulphuric acid as a homogeneous catalyst.
- Direct hydration of propylene using a heterogeneous catalyst. This reaction may take place in the vapour phase, the liquid phase or a vapour-liquid mixture.

Each process and its major effluents and wastes is described below.

Indirect hydration of propylene

This process produces isopropyl alcohol and four other solvents (di-isopropyl ether, di-methyl ketone, secondary butyl alcohol, and methyl ethyl ketone). Propylene and butylenes in mixed C3 streams and mixed C4 streams are reacted with 70-75% sulphuric acid to form the corresponding alkyl sulphates, which are subsequently hydrolysed to the corresponding alcohols. The related ethers are formed as by-products.

The crude alcohols are purified by distillation to give an isopropyl alcohol azeotrope with water and relatively pure secondary butyl alcohol. These may be sold or converted to the related ketones by dehydrogenation over a brass catalyst.

Potential emissions to air:

 Oxides of carbon, oxides of nitrogen and oxides of sulphur from the incineration of waste process gases; hydrocarbons from tank vents, strippers, condensers, and reaction time tanks; isopropyl alcohol from the cooling tower; chromium from the incineration of solvent slops; and nickel from the incineration of caustic sludge.

Potential emissions to water:

 Alcohols, ketones, furfural, copper and zinc from aqueous interceptor discharges, spent sulphuric acid and caustic soda.

Potential solid waste streams:

- Spent brass catalyst if not regenerated.
- Ash from incinerator.

Direct hydration of propylene

The propylene feed is purified first by distillation to remove propane. Propylene is then hydrated in the vapour phase.

The major by-product is di-isopropyl ether; other by-products include n-propanol, acetone, hexanol and low molecular weight polymer. The reaction takes place at approximately 180°C and 34 barg over a catalyst of 42-46% phosphoric acid on porous clay beads.

The product is water scrubbed to separate the isopropyl alcohol. Unreacted propylene is recycled, a purge being taken to prevent propane buildup. Isopropyl alcohol is purified by distillation, finally azeotropically using cyclohexane as an entrainer.

Potential emissions to air:

Hydrocarbons from tank and process vents and fugitive emissions of hydrocarbons.

Potential emissions to water:

• Propanols, organic phosphates and inorganic phosphates from water wash.

Potential solid waste streams:

Phosphoric acid and phosphates as spent catalyst.

Emissions controls

Management Raw

materials

Techniques for pollution control Waste Waste handling recoverv or disposal

Emissions Energy

Closure

Installation issues

2.1.3.3 OXO alcohols

OXO alcohols range from butanols (C4) to C20 alcohols. There are two basic variations to the manufacturing process from olefins, one based upon hydroformylation and the other upon carbonylation followed by hydrogenation.

Hydroformylation

Synthesis gas, used as one of the feed materials for this process route, may be produced by reforming naphtha or natural gas. Liquid naphtha is desulphurised by hydrogenation at 400°C and 20 barg. over a nickel catalyst and the hydrogen sulphide thus formed removed on iron oxide/zinc oxide absorbers. The treated naphtha is then mixed with steam and recycled carbon dioxide and fed to a reformer, for treatment at 850°C and 17.5 barg over a nickel-based catalyst. Carbon monoxide and hydrogen are produced in an endothermic reaction, with carbon dioxide and methane as by-products. Part of the product stream is scrubbed to remove carbon dioxide

For normal butyl alcohol manufacture synthesis gas is fed, with propylene and catalyst to a reactor system. After reaction at 170°C and 70 bar g. gases, mainly unreacted propylene and synthesis gas, are removed to leave a mixture of catalyst in alcohol which is then distilled to produce a crude normal butyl alcohol. This is purified by distillation and azeotropic distillation to separate isobutyl alcohol from the product.

C7-C15 Alcohols are produced from the respective olefins by combination with synthesis gas. The reaction takes place at 180 to 200°C and 50 barg over catalyst. After depressuring and recycling of evolved gas the crude product is distilled under vacuum. The crude alcohol is treated with caustic soda to saponify byproduct formates, water washed and then distilled to remove unreacted olefins, byproduct paraffin hydrocarbons and heavy fractions. Finally, the alcohols are hydrogenated at elevated temperature and pressure over a nickel catalyst to remove the last traces of aldehydes.

Potential emissions to air:

- Oxides of carbon, oxides of nitrogen and oxides of sulphur from the incineration of process waste gases and plant ejector vents.
- W-butanol and mixed hydrocarbons from plant ejector vents and sludge incineration.

Potential emissions to water:

Suspended solids, butanols, aldehydes and butyl formate from contaminated process aqueous effluent.

Potential solid waste streams:

Zinc oxide, cobalt, molybdenum, chromium oxide, iron oxide, copper oxide and activated carbon from the desulphurisation and converter catalysts and activated carbon absorbers.

Carbonylation and hydrogenation

The liquid olefins are reacted with carbon monoxide and hydrogen in the correct proportions at 145°C and 260-270 barg to give liquid aldehydes, and by-products including heavy ends resulting from aldehyde side reactions. After separation from the carbon monoxide and hydrogen, which are recycled, the aldehydes are vaporised with hydrogen and hydrogenated to give the corresponding alcohol. The alcohol is cooled, separated from the hydrogen and purified. Purification is by distillation to remove unreacted olefins, methanol, water and heavy ends.

Potential emissions to air:

- Oxides of carbon from the catalyst letdown vessels and reactor blowdown.
- Alcohols from hydrorefiner vents.

Potential emissions to water:

Hydrocarbons in ejector condensate.

Introduct	ion		Techniques for	pollution control		Emissions			Impact			
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

Methanol in wash waters.

Potential solid waste streams:

Spent catalyst.

2.1.3.4 Formaldehyde

A more detailed description of formaldehyde processes is given in the BREF (pp. 247-265). Formaldehyde is manufactured by two main processes:

- Silver catalytic oxidation of methanol In the silver catalytic oxidation route the methanol is reacted with oxygen over a silver catalyst, at atmospheric pressure and a temperature of 600-650°C. Side reactions are minimised by cooling rapidly to 500°C.
- Metal oxide catalytic oxidation of methanol In the metal oxide route, the same raw materials are
 used, but the catalyst is an iron molybdenum compound. Performance enhancement is achieved by
 adding small amounts of other metal oxides, for example chromium oxide. The reaction takes place
 at atmospheric pressure and at temperatures of 300-400°C. The metal oxide process accounts for
 the majority of recently constructed installations, and a simplified flowsheet is shown in Figure 2.4
 below.

Potential emissions to air:

- Absorber tail gas with formaldehyde and related organics. This is usually destroyed by thermal (silver process) or catalytic oxidation.
- Fugitive emissions from equipment and fittings; high integrity pumps and minimal flanges are used on some plants internationally.
- Evaporative losses of formaldehyde and methanol from tanks and transfer; wet scrubbing can be used.

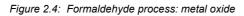
Potential emissions to water:

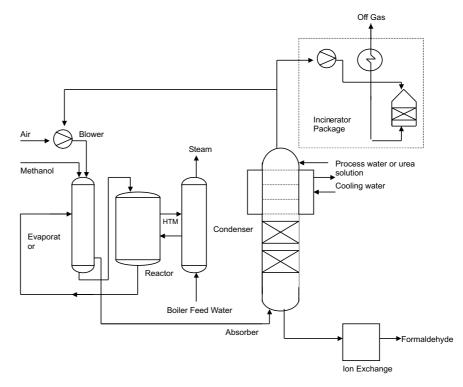
Contaminated condensate and washwater.

Potential solid waste streams:

• Spent catalyst.

Introduction		Techniques for	pollution control		Emissions			Impact			
In-process controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	





2.1.3.5 Formic acid

Four methods are used to produce formic acid:

- · By-product of acetic acid manufacture.
- Methyl formate route.
- · Methyl formate via formamide route
- Sodium formate route

In the UK, large scale manufacture of formic acid is as a by-product of acetic acid manufacture by liquid-phase catalytic oxidation. Refer to Section 2.1.2.6 below.

2.1.3.6 Acetic acid

There are two main methods for the manufacture of acetic acid:

- Liquid phase catalytic oxidation
- Methanol carbonylation

Liquid phase catalytic oxidation of light hydrocarbons

This method involves the liquid phase catalytic oxidation in air of light hydrocarbons at a temperature between 150-200°C and a pressure between 40-50 barg. The aqueous reaction product is purified in a series of distillation columns producing acetic, formic, and propionic acids and acetone. Lean off-gas from the reactor is dried and then recovered in activated carbon beds. Remaining gas is fed to a thermal destruction unit.

Potential emissions to air:

- The light hydrocarbon off-gas from the activated carbon beds/thermal destruction unit.
- Acetic acid, acetaldehyde, acetone, carbon monoxide and other organics from vacuum pump discharges.
- Scrubbed vent gases from the acetone recovery unit containing acetone, methyl acetate, benzene, acetic acid, methyl ethyl ketone, esters, methanol and some high-boiling components.

Special control techniques include:

 Thermal oxidation of reactor off-gas, including recovery of heat and power by use of off-gas expanders and waste heat recovery.

Potential emissions to water:

- Acetic acid, ketones, methanol and acetaldehyde from vacuum systems.
- Final residues of butyric and succinic acids, aqueous streams from the distillation unit.
- Water from the acetone recovery unit containing methanol, ethanol and traces of acetone and sodium salts.
- A discharge from the hydro-extractive distillation of propionic acid containing propionic acid, acetylacetone and 2,4 hexadiene.

Potential solid waste streams:

- · Waste from driers, activated carbon beds and catalyst systems.
- Corrosion products containing a glass lead mixture contaminated with nickel oxalate and oxides of chromium and iron.

Methanol carbonylation

One process variant involves the use of a pressure of 700 barg, and Hastelloy C as the construction material with coper/cobalt/cobalt catalyst systems in the presence of iodine. The other process variant is based on the use of rhodium/phosphine complexes as the catalyst system, together with hydrogen/ methyl iodide as promoter. Operating pressures of 33 - 36 barg and temperatures of 150 - 200°C are utilised. Purification involves multiple distillation to remove the catalyst mixture, water, mixed acids and other impurities.

Potential emissions to air:

- High pressure off-gas from the reactor which is absorbed and scrubbed in a light ends recovery system before venting to a thermal destruction unit and contains small quantities of hydrogen iodide.
- Flared light ends from the first two distillation columns which pass via a low pressure absorber system containing chilled acetic acid before being vented to a thermal destruction unit, again containing small quantities of hydrogen iodide.

Special control techniques include:

· Offgas scrubbers, using methanol or acid recycled back to the process.

Potential emissions to water:

- Liquor from iodine scrubber during catalyst addition.
- Liquor from the final column light ends scrubbers contaminated with acetic acid.

Potential solid waste streams:

 Heavy fractions from the heavy acids column, comprising propionic and acetic acids together with potassium salts and catalyst.

2.1.3.7 Acetic anhydride

There are two main methods for the manufacture of acetic anhydride:

· Acetic acid/ketene route (positive or reduced pressure cracking).

Introduction	Techniques for	or pollution contro	I	Emissions			Impact			
In-process controls Emissions Manag	ment Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

Carbonylation of methyl acetate.

The acetone/ketene route is not currently used in the UK.

Acetic acid/ketene

The first stage is the catalytic endothermic decomposition of acetic acid to give ketene and water. A temperature of 700°C and reduced pressure are used. Alternatively positive pressure may be used. Product vapours from the process comprise ketene, some unreacted acetic acid and by-products.

The second stage involves the addition of ketene to acetic acid under reduced pressure to give acetic anhydride. Acetic anhydride is recovered by distillation.

Carbonylation of methanol

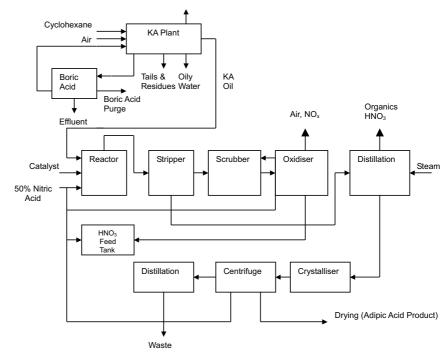
This process involves the esterification of methanol with acetic acid (possibly from a recycle source) or a portion of the product acetic anhydride, to produce methyl acetate. Carbonylation of methyl acetate yields acetic anhydride. This route is associated with the carbonylation of methanol to acetic acid (see Section 2.1.2.6).

2.1.3.8 Adipic acid

The commercial manufacture of adipic acid is achieved in two stages. The first stage is either the oxidation of cyclohexane or the hydrogenation of phenol to give a cyclohexanone/cyclohexanol mixture (known as KA or ketone-alcohol), which is purified by distillation. The catalyst is recycled via a crystallization system. In the second stage KA is oxidised with nitric acid. The catalyst is a copper salt. The process emits substantial quantities of nitrous oxide (N2O), which has a high global warming potential. Purification of adipic acid involves crystallisation and centrifuging.

A simplified process flow diagram is shown in Figure 2.5.

Figure 2.5: Adipic acid procuction



Potential emissions to air:

Introduction	Techniques for	pollution control		Emissions			Impact		
In-process controls Emissions Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

- Oxides of nitrogen and nitrous oxide from the stripping columns and crystallisers.
- · Adipic acid particulate from drying and handling.
- · Other organics from feedstock and absorbers and purification columns on the KA section.
- Caproic, adipic, valeric, butyric, propionic and acetic acids (all of which have pungent odours) from acid handling and storage.

Special control techniques of relevance to adipic acid production focus on the abatement of the stream containing nitrous oxide. Techniques used internationally include catalytic treatment and thermal destruction in reducing conditions with methane.

Potential emissions to water:

- KA catalyst and organics from KA purification
- Oily water
- Low pH waste streams containing adipic, boric, glutaric and succinic acids with copper, vanadium and sulphuric acid.

Special control techniques include:

- · Ion exchange systems to remove inorganic salts, such as copper or vanadium salts from catalysts.
- Evaporation and crystallisation to recover boric acid and other by-products.

Potential solid waste streams:

- KA catalyst from plant cleaning
- Non-volatile organic residues and organic recovery tails from KA production.
- Wastes on shut-down: tar-contaminated sand, oxidiser residues, KA sump dredgings.
- Boric acid sweepings.
- Caustic wash residues.

2.1.3.9 Methacrylic acid

There are two main routes for the manufacture of methacrylic acid:

- Acetone cyanohydrin process
- Vapour phase catalytic oxidation from isobutylene or tertiary butanol

Of these, only the acetone cyanohydrin process is employed in the UK.

The acetone cyanohydrin process comprises five process stages **Figure 2.6**. The first, conversion of the cyanohydrin to an amide, is undertaken in a stirred reaction vessel. From there the reactants pass to a hydrolyser where the amide is hydrolysed to methacrylic acid which is then recovered in a phase separator. The methacrylic acid passes forward for purification by distillation and the remainder by-product acid is distilled. Organic material is recovered for recycle and spent acid can be recovered via an acid recovery plant if available.

Potential emissions to air:

- Vent gases from the by-product acid separator.
- Vent gases from the reactor and hydrolyser containing carbon monoxide, sulphur dioxide, and
 organic compounds, including Methacrylic acid.

In one control technique, fuel rich vent can be sent to a vent gas burner, for destruction to CO_2 , NO_X and N2.

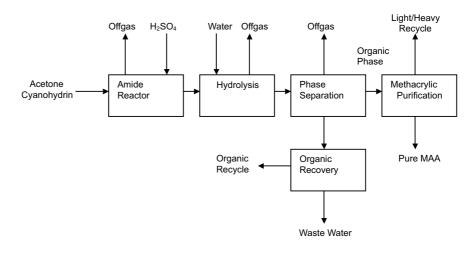
Potential emissions to water:

- Waste streams from vacuum systems containing organics.
- Waste water from the organics recovery unit

Introduction		Techniques for	pollution control		Emissions			Impact			
In-process controls Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

Special control techniques include the recovery of organics from purge water.

Figure 2.6: Manufacture of methacrylic acid



2.1.3.10 Phthalic anhydride manufacture

Phthalic anhydride is manufactured by fixed bed oxidation. In this process ortho-xylene or naphthalene and air are preheated and passed through the catalyst chamber. The reactor gases are subsequently cooled and passed through switch condensers where the crude product de-sublimes. The off-gases are either scrubbed or incinerated before discharge to the atmosphere. Crude product is distilled under vacuum to achieve the required purity. The following discharges relate to the ortho-xylene route.

Potential emissions to air:

- Off-gas from the switch condenser scrubber, containing phthalic anhydride, maleic anhydride, various acids, sulphur dioxide, phthalide and carbon monoxide.
- Combustion products from incinerated residues and overheads from the distillation columns.

Potential emissions to water:

 Acidic scrubber liquor from the switch condenser off-gas scrubber or wastewater from maleic anhydride recovery.

Potential solid waste streams:

· Solid organic residues from distillation columns and stills.

Special control techniques include:

- Wet scrubbing of switch condenser off-gases, with recovery of maleic anhydride by processes such as azeotropic dehydration.
- Catalytic incineration of scrubber tail gas, or condenser off-gas if no scrubber is installed.
- Incineration or fuel use of all hydrocarbon residues.

2.1.3.11 Propionic acid manufacture

There are two main methods for the manufacture of propionic acid:

- By-product of acetic acid manufacture.
- The OXO process.

Introduction	1		Techniques for	pollution control		Emissions			Impact			
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

Current UK production is via acetic acid manufacture. Refer to section 2.1.2.6 for further details.

2.1.3.12 Terephthalic acid manufacture

Terephthalic acid is manufactured in a two step process; first para-xylene is oxidised in acetic acid to produce a crude terephthalic acid. This is followed by selective catalytic hydrogenation of the crude product, to allow a purified terephthalic acid to be recovered. Both the oxidation and the purification steps employ crystallisation of the reaction products, followed by solid/liquid separation (by centrifuge or filter) and drying of solids to recover pure terephthalic acid (PTA) from the process solvents and other more soluble organic acids and aldehyde by-products.

Potential emissions to air:

- Off-gases from the oxidation stage containing carbon monoxide, acetic acid, methyl acetate, paraxylene and methyl bromide.
- Vent gases from solvent recovery column containing carbon monoxide, methyl acetate, paraxylene and acetic acid
- · Vent gases from the atmospheric absorber containing acetic acid and methyl acetate.
- Vent gases from purification plant scrubber containing terephthalic and acetic acids.
- · Vent gases generated from the off-gas driers containing methyl acetate, acetic acid and paraxylene.

Potential emissions to water:

- Aqueous condensate from solvent recovery and acetic acid dehydration columns containing acetic acid, formaldehyde, methyl acetate, paraxylene and methanol.
- Waste water from crude terephthalic acid purification stage containing paratoluic, terephthalic, benzoic, and other organic acids, together with manganese and cobalt salts.
- Aqueous condensate from the residue treatment crystalliser steam eductors.
- · Washings from rotary vacuum filters, centrifuges and other process equipment.

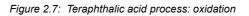
Potential solid waste streams:

• Filter cake from residue recovery area.

Special control techniquesinclude:

- Solids including by-product organic acid and traces of catalyst recovered as a solid residue.
- Optimisation of the reactor conditions to minimise by-product production.
- Lagoons to cope with high BOD loads resulting from washings of equipment, or operational problems caused by process blockages.

Introduction		Techniques for	pollution control		Emissions			Impact			
In-process controls Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring		Installation issues	



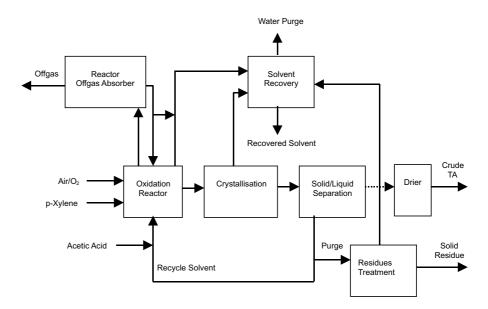
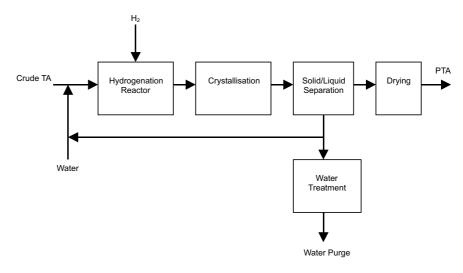


Figure 2.8: Teraphthalic acid process: purification



2.1.3.13 Vinyl acetate

Vinyl acetate can be produced from acetylene and acetic acid. In the UK, vinyl acetate is produced only from ethylene, acetic acid and oxygen. Carbon dioxide, water, acetaldehyde, ethyl acetate and higher esters are formed as by-products. The reaction takes place in the vapour phase at 160°C and 8 barg over a noble metal catalyst of palladium and gold and potassium acetate supported on silica beads. The product is quenched, carbon dioxide is removed using hot potassium carbonate and unconverted oxygen and ethylene recycled. A purge stream prevents inert buildup. Unconverted acetic acid is separated from the crude product by distillation and recycled. The vinyl acetate is purified in a series of distillation columns.

Potential emissions to air:

Hydrocarbons from the reactor loop purge.

Introduction		Techniques for	pollution control		Emissions			Impact		
In-process controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

Carbon dioxide from the absorption/desorption system.

Potential emissions to water:

Sodium acetate in the neutralised aqueous effluent from water stripping.

Potential solid waste streams:

None (assuming high boilers, light ends etc. are used as fuel).

2.1.3.14 Acrylates

Manufacture of methyl methacrylate

There are two principal routes for the production of methyl methacrylate (MMA); oxidation of C4 hydrocarbons, and hydrolysis and subsequent esterification of acetone cyanohydrin (ACH). Only the ACH route is currently used in the UK.

Methyl methacrylate is produced from acetone cyanohydrin (ACH) in a continuous process comprising three stages - amide production, esterification and distillation.

The amide, methacrylamide sulphate, is produced by the action of strong sulphuric acid on ACH. Typically there are two reactors in series. In the first the reaction is exothermic, and so requires cooling, whilst the second is endothermic and so requires heating. Unwanted decomposition products include carbon monoxide.

The resulting amide is fed to esterification vessels where methanol and water are added. The reaction is exothermic. Steam is added to drive off organic vapour from the vessels. The liquid then passes to a stripping section for the removal of organics from the aqueous residue, the majority of which is sulphuric acid. The vapour is condensed and resulting liquid separated. The aqueous phase is returned to the esterifier, whilst the organic phase is passed to a storage tank for crude MMA. The aqueous waste streams containing sulphur may be directed to a sulphuric acid recovery plant.

The crude MMA is purified by distillation. The light fraction can be incinerated and the heavy fraction is recycled back to the esterifier, water passes to the effluent system. A stabiliser is added to the MMA. The stabiliser in MMA needs oxygen to function and the MMA is accordingly stored under air.

Potential emissions to air:

- Carbon monoxide, sulphur dioxide and organics from the amide reactor vent.
- · Carbon monoxide, sulphur dioxide from the condenser on the esterifier.
- Hydrocarbons from the distillation column.
- · Methyl methacrylate from the storage tanks.
- Methyl methacrylate from vacuum pump discharge.

Thermal destruction should be considered for all these streams.

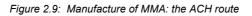
Potential emissions to water:

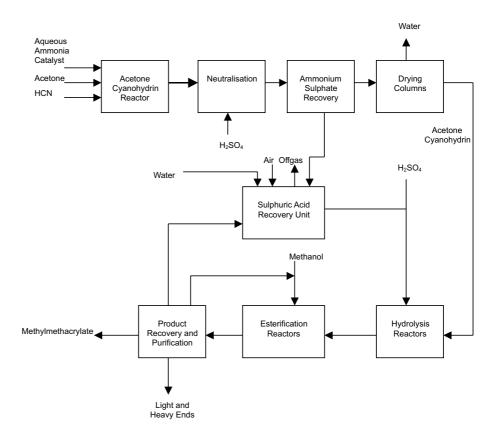
- Sulphuric acid, ammonium sulphate, sulphonated tars from the esterifier.
- Dimethyl ether, methanol, acetone, MMA, from the vacuum pump seal water and the column water fraction.

Potential solid waste streams:

- Carbonaceous fouling from the esterifier vessel
- Methacrylate polymer removed from the esterifier during shut-down.

Introduction	Techniques for pollution control			Emissions			Impact		
In-process controls Emissions controls Mar	 Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring		Installation issues





Manufacture of hydroxy acrylic monomers

These are produced from the reaction of ethylene oxide and propylene oxide with methacrylic or acrylic acid in processes comprising epoxidation of the acrylic/ methacrylic acid and distillation.

Crude hydroxy acrylates and methacrylates are produced in a batch process. Methacrylic or acrylic acid is charged to the reactor with the appropriate catalyst -a heavy metal based organo-metallic compound - and then the ethylene oxide or propylene oxide is progressively added. The reaction is initiated by heating and, as the exothermic reaction progresses, cooling is applied to maintain the desired reaction temperature.

After reaction, when the pressure has fallen to 2 bar, the contents are transferred into a vessel where they are sparged with a mixture of nitrogen and air and vacuum treated to reduce the oxide level.

Vapours from the vacuum pump are condensed. Remaining gases, along with vapours from the sparging vessel, are vented through a water scrubber where the residual oxide is absorbed.

The crude acrylate is transferred into atmospherically vented tanks which are aerated with small amounts of air. The crude acrylate is then purified by distillation to remove traces of the organo-metallic catalyst.

Both acrylic and methacrylic acid are stored in heated tanks. The acids are inhibited to prevent polymerisation and air is bubbled through to maintain activity of the inhibitor.

Potential emissions to air:

- Ethylene or propylene oxide from storage tanks.
- · Acrylic and methacrylic acid from storage tanks.
- · Ethylene or propylene oxide, acrylates from the vacuum pump.
- Ethylene or propylene oxide from charging of pre-mix vessel and reactor.

Introduction		Techniques for pollution control			Emissions			Impact		
In-process controls Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

Potential emissions to water:

- Ethylene or propylene oxide in scrubber effluent.
- Ethylene or propylene oxide, acrylates in condensed steam and cooling water.
- Catalyst in distillation column effluent.

Potential solid waste streams:

- Acrylates and catalyst adduct in distillation bottoms.
- · Polymer from reactor and distillation column cleaning
- Spent catalyst.

2.1.3.15 Ethylene oxide

A more detailed description is given in the WOC BREF (pp. 221-246).

Ethylene oxide is manufactured by the oxidation of ethylene over a silver-based catalyst. Although ethylene oxide can be produced by an air-based process, most modern processes are oxygen-based. The reaction at 250°C is exothermic, with the heat of reaction being removed by raising steam. The reactor effluent is cooled, passed to an absorber and the quenched gas contacted with water to recover the products as a dilute aqueous solution. This solution is heated and the product separated by steam stripping. Unreacted ethylene is recycled to the reactor and the by-product ethylene glycol is fed directly to an ethylene glycol plant. Ethylene oxide is purified by distillation. Part of the recycled gas (about 20%) is treated to remove significant quantities of carbon dioxide, generated in the oxidation process, before return to the reactor.

Potential emissions to air:

- Oxides of carbon and hydrocarbons from loop purges and the carbon dioxide absorber vent.
- Ethylene oxide from the reactor analyser vents, the purification process and storage vents.
- Small amounts of ethylene dichloride, which is used in small quantities to modify the oxidation reaction, are also released.

Special control techniques include:

- Flash unit to recover hydrocarbons from the CO₂ absorber liquors.
- Refrigerate EO storage.
- Ground level flare for the reactor purge loop.

Potential emissions to water:

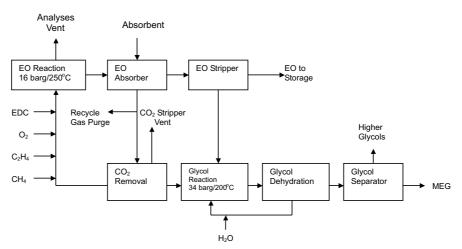
- Ethylene glycol from ethylene oxide quench purges and carbon dioxide absorber purges.
- Sodium salts from ethylene oxide quench purges; potassium salts from carbon dioxide scrubber purges.
- Aldehydes from aldehyde purges.

Potential solid waste streams:

None.

Introduction	Techniques for	Techniques for pollution control			Emissions			Impact		
In-process controls Emissions controls Managemen	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

Figure 2.10: Ethylene oxide/etheylene glyco production



2.1.3.16 Ethylene glycol

Ethylene glycol (MEG) is produced from ethylene oxide and water, and a detailed description is given in the EO/glycol section of the BREF (pp221-246). Higher glycols are produced as by-products; the most significant being diethyleneglycol (DEG). The ethylene oxide is mixed with excess water and hydrolysed at above 190°C. The ethylene glycol is purified by distillation with recycling to improve recovery. Further ethoxylation of the DEG yields tri- and tetra- ethylene glycol.

A combined ethylene oxide and ethylene glycol plant is shown in Section 2.1.2.15.

Potential emissions to air:

• Vents and purges from process streams.

Potential emissions to water:

Glycols may be released in ejector condensate and purge streams.

Potential solid waste streams:

None.

Special control techniques include:

Minimisation of water purges by recycling.

2.1.4 Organic compounds containing sulphur

2.1.4.1 Carbon disulphide

Carbon disulphide is manufactured by the reaction of sulphur and hydrocarbons such as methane, ethane, propylene or natural gas. The gas is usually preheated and then mixed with vaporised sulphur. The mixture is then heated to between 580-650°C and pressures between 2.5-5 barg. to produce carbon disulphide and hydrogen sulphide. Uncondensed carbon disulphide is recovered from the

Introduction			Techniques for pollution control			Emissions			Impact		
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

hydrogen sulphide by absorption in odourless kerosene, followed by steam stripping, and the combined carbon disulphide streams are purified by distillation. The hydrogen sulphide is converted back to sulphur in a Claus plant.

Potential emissions to air:

- Combustion products from natural gas used in furnaces. A white plume and brown cloud can be generated if there is a furnace tube failure.
- •
- Oxides of sulphur from combustion of carbon disulphide and hydrogen sulphide, stripped by steam from the stabiliser feed drum overflow and sent to the flare system.
- The gases leaving the absorber column contain hydrogen sulphide, sulphur and carbon disulphide. After passing through a wire-mesh filter to remove entrained droplets the gases are passed to a Claus unit to recover sulphur.
- The carbon disulphide surge tank vent is blanketed with methane (natural gas) leading to a continuous discharge to the flare system. This may be contaminated with carbon disulphide.
- Compressed air is used to strip out carbon disulphide from the surge tank catch pot overflow. This
 may form a stream containing a significant concentration of carbon disulphide which requires treatment.
- Odourless kerosene from the production plant may be used to absorb carbon disulphide vapours emitted during the filling of tankers.
- Pipework from the sulphur condensers discharges to a flare stack. During furnace start up a methane feed is established, and sulphur feed is slowly increased until the desired conversion is achieved.

Potential emissions to water:

- The aqueous layer from the stabiliser feed drum is degassed with steam and passed to a catch pot to which cold water is added.
- A purge of the lean oil system is completed to prevent the build up of sulphur compounds. This is stripped using a polysulphide caustic liquor.
- Following aeration with compressed air, the surge tank catch pot overflow discharges to the site effluent drains.
- Spillage into the tanker loading sump is not normal and therefore water displaced by rainfall is generally the only discharge from this source.

Potential solid waste streams:

• The sulphur filters are coated with diatomaceous earth. This, together with some sulphur and inorganic impurities, is removed at intervals.

2.1.4.2 Dithiocarbamates

An aqueous alkaline solution of secondary or tertiary amines is reacted with carbon disulphide to form aqueous dithiocarbamates.

Aqueous dithiocarbamates can be added to an aqueous metal salt to produce a slurry of the metal dithiocarbamate. The dithiocarbamate is then filtered and dried. Zinc, nickel and copper dithiocarbamates are the main products.

2.1.4.3 Thiols

Some of the preferred methods for manufacturing thiols are outlined below.

Management

Raw

materials

Techniques for pollution control Waste handling

Waste

disposal

Installation issues

Closure

Ethanethiol is prepared by the vapour-phase reaction between ethylene and hydrogen sulphide over an acid catalyst. Methanethiol is similarly prepared from the corresponding alcohol.

Accidents

Other primary thiols are prepared by the UV-light promoted addition of hydrogen sulphide to primary alkenes. This reaction occurs in the liquid phase, with a free radical mechanism. Medium pressure mercury lamps, or other free radical generators such as azonitriles are used as promoters. Excess hydrogen sulphide is used to minimise the formation of by-products such as the addition product of thiol and alkene.

Tertiary alkane thiols are prepared from the corresponding tertiary alkene and hydrogen sulphide, in a continuous flow reaction over a solid catalyst. For example, 2-methyl-2-propanethiol is made from isobutylene. Catalysts used include aluminium chloride, other acid halides, hydrogen fluoride and boron trifluoride.

Thiophenol is prepared by the red phosphorus reaction of benzenesulphonyl chloride. Another route is the high temperature reaction of monochlorobenzene and hydrogen sulphide.

Thiols are transported as liquids - they are flammable and volatile. Process equipment and storage vessels should be constructed of carbon seel, aluminium, stainless steel or other copper-free alloy. Thiols stored in carbon steel should be kept dry and blanketed with an inert gas to prevent the formation of iron-sulphur complexes. Rubber is not suitable for hoses or gaskets.

Potential emissions to air:

- As a result of opening drums for transfer of contents to reactors, vapours are emitted which are usually locally extracted. These are usually passed either to carbon adsorbers or, if available, to a lean gas main and incinerated.
- Used drums are sent to a drum decontamination plant where they are slightly heated. The extracted vapours are adsorbed or if appropriate collected in a lean gas main for incineration or alternatively caustic scrubbed.
- Blending tanks are vented either to a carbon adsorber or, if appropriate, to a lean gas line for incineration or caustic scrubbed.
- Road Tankers are equipped with a carbon adsorber to remove residual odours.
- Spent tanker wash down methanol is usually incinerated.

Potential emissions to water:

The final water flushing of tankers containing unspent hypochlorite is discharged to effluent treatment.

Potential solid waste streams:

- Spent caustic solution from backup incinerator scrubbers is usually landfilled.
- Sludges and filter cakes from effluent treatment containing dithiocarbomates, and other sulphur compound complexes are sent to landfill.

2.1.4.4 Thiophene

There are three commercial processes for the production of thiophene.

Furan and hydrogen sulphide

The vapour-phase reaction between furan and hydrogen sulphide over a heteropoly acid-promoted metal oxide catalyst at 300-400°C gives thiophene and water as reaction products. These are separated and crude thiophene is continuously distilled to produce a high purity product. The catalyst has a long service life and does not need periodic regeneration. The same process can be used to manufacture 2-methylthiophene from 2-methylfuran, and tetrahydrothiophene from tetrahydrofuran.

Emissions controls

Raw materials

Management

Techniques for pollution control Waste Waste handling recovery of disposal

Emissions Energy Accidents

Noise

Installation issues

Closure

C4 compounds and carbon disulphide

C4 raw materials (1-butene, butadiene, n-butanol and 2-butenal) undergo continuous reaction with carbon disulphide over an alkali-promoted metal oxide catalyst at 500°C. Yields vary according to the starting material. The catalyst must be periodically regenerated to remove surface coke build-up. The process may be used for the manufacture of 2- and 3-alkyl thiophenes.

Butane and sulphur

This process involves the continuous reaction of butane and sulphur at 500-600°C over a mixed metal oxide catalyst. The hydrogen formed reacts exothermically with the sulphur feed to give hydrogen sulphide. Hydrogen sulphide then reacts with butane residue to yield thiophene. Periodic air regeneration of the catalyst is required. The process may also be applied to the production of 2- and 3-alkyl thiophenes from higher hydrocarbons.

2.1.4.5 Ethyl pentachlorothiophene

Phosphorus pentasulphide and ethanol are reacted together to form diethyldithiophosphoric acid (DETA). Hydrogen sulphide is liberated in this process. If the reactor temperature were allowed to rise to 150°C, ethyl thiol would be generated. Ethanol is used to scrub the reactor vent gases before entering the reactor. EPCT is produced by chlorination of DETA when sulphur is precipitated. The hydrogen chloride liberated is adsorbed and residual gasses passed through a caustic scrubber to an incinerator. EPCT is distilled off into a second receiver leaving the heavier residues in the distillation still. Prolonged distillation can lead to additional thiols being generated.

Potential emissions to air:

- Breathing emissions from the ethanol storage tank are released directly to the atmosphere.
- Off-gases from the reactor are incinerated with contaminated combustion air drawn from the building caustic scrubber discharge and storage tank vents.

Potential emissions to water:

- Spent scrubber liquor is discharged frequently.
- 32% hydrochloric acid is generated in the adsorber (water scrubber) from hydrogen chloride fumes. This is usually sold commercially or can be used to neutralise alkaline liquid waste streams from elsewhere on site.

Potential solid waste streams:

- Cartridges from the DETA filter are collected and sent for off-site disposal.
- The residues generated in the chlorination are discharged to steel drums loaded on a conveyor. Operators are protected by screens through which the building ventilation air is drawn into the tunnel and to the incinerator. Drums are allowed to cool before lidding and are sent to landfill.

2.1.4.6 Mercaptobenzothiazole

Mercaptobenzothiazole (MBT) is produced by the reaction between aniline, carbon disulphide and sulphur and produces hydrogen sulphide as the main by-product. Other by-products include aminophenols, thiocarbonilides and anilidobenzothiazoles ie. Benzothiazole (BZT).

MBT is a solid product handled in the form of dry preformed pellets which are generally non-dusty.

MBT is produced in a batch reaction. Sulphur is charged from hot molten bulk storage and carbon disulphide and aniline from bulk storage. The reaction is carried out at over 200°C and greater than 50 barg. The hydrogen sulphide produced must be released from the reactor system under pressure control.

At the completion of the reaction the BZT and any remaining aniline is steam distilled and separated overhead, with the aqueous condensate phase being a waste stream. The organic condensate phase is recycled. Product from the still is sent to storage and the tarry residues are generally drummed off for disposal.

2.1.4.7 Special considerations for organic sulphur compounds

The following sections are relevant to most processes involving organic chemicals containing sulphur.

Potential emissions to air:

- The low odour thresholds of many sulphur compounds has resulted in the wide use of technologies designed to minimise emissions such as all welded pipework, canned pumps, scrubbing equipment etc.
- Waste process gases are likely to contain hydrogen sulphide and should, where practicable, undergo sulphur recovery. A typical sulphur recovery unit is described in section 2.1.3.8.
- During normal operation, waste streams from carbon disulphide processes are adsorbed in odourless kerosene. The resulting stream containing hydrogen sulphide, sulphur and carbon disulphide could be incinerated to give sulphur dioxide as well as carbon oxides and water vapour. Methods to minimise the release of sulphur oxides should be considered. Where appropriate sulphur recovery units should be installed upstream of any incineration equipment.
- Contaminated extraction air can be dealt with most easily by incineration. Otherwise, carbon or biological filters may be considered. Amine, caustic scrubbing or other systems may be appropriate for particular emissions.
- Odour problems are particularly prominent in the manufacture of thiols and other organic sulphur compounds. Adsorption beds and biofilters may be used to eliminate odours from fugitive emissions in enclosed areas.

Potential emissions to water:

- Liquid effluents will originate from scrubbing systems, process wastes and from routine cleaning of equipment. The effluents may contain carbon disulphide, or hydrogen sulphide, mercaptans or other organic sulphur compounds.
- Effluents are likely to require primary and secondary treatment prior to discharge to the environment.
- Aqueous wastes contaminated with kerosene (carbon disulphide process) will require oil separation. Where possible contaminated kerosene should be regenerated on-site by stripping with a polysulphide caustic liquor.
- Spent scrubber liquors can be treated with hypochlorite to form inert chlorates of sulphur. The use of hypochlorite or other easily handled oxidant (such as hydrogen peroxide or ozone) should be considered for the elimination of odours in effluent.

Potential solid waste streams:

• Wastes intended for disposal to land are likely to contain organic sulphur compounds. Operators should ensure that these compounds are removed prior to the landfill of wastes or that the wastes are suitably contained to prevent the release of the sulphur component.

Introduction	Techniques for	Techniques for pollution control			Emissions			Impact		
In-process controls Emissions controls Management	nt Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

emissions to land may include spent consumables from the process such as drums, sacks and rags. These may be contaminated with sulphur compounds and therefore generate odours.

2.1.4.8 Sulphur recovery

Sulphur is usually recovered from gas streams containing hydrogen sulphide by absorption of the H2S in specialist solvents, from which a stronger H2S stream can be generated by heating. A claus plant then oxidises the H2S to sulphur.

Hydrogen Sulphide scrubbing

There are several recovery techniques currently employed in the LVOC sector utilising scrubbing type processes. Examples include:

Ethanolamine processes:

- Mono and di-ethanolamines readily adsorb hydrogen sulphide and carbon dioxide which can be
 released by heating and pressure reduction. The amine adsorbent passes counter-current to the
 sour gas in a packed column and sweetened gas passes for further treatment. The rich amine
 stream is transferred to a feed drum which also separates entrained hydrocarbons. I then passes to
 a regenerator column where heat is applied to drive off the hydrogen sulphide. The overheads are
 cooled with condensate being recycled to the column and the acid gas (greater than 90% hydrogen
 sulphide) is passed to the sulphur recovery unit and the lean amine stream is recycled to the scrubber.
- Methyldiethanolamine (MDEA) features in many of the most modern amine blends. They have a good absorption efficiency and can be tailored to suit particular waste streams.

Hot carbonate process:

 This process utilises the same operations as the MDEA process except that the adsorbent is potassium carbonate.

Sulfinol process:

 In order to avoid the degradation losses suffered by MDEA solutions, some plants have switched to the solvent Sulfinol. The Sulfinol solution usually consists of 40-45 wt.% sulfolane (tetrahydrothiophene dioxide), 40-45% diisopropanolamine, and the balance water. Sulfinol provides greater gas-treatment capacity, lower solvent circulation, lower heat requirements, and lower rates of solvent degradation.

Alkazid process:

 The alkazid process is a cyclic heat regenerative type. It uses a solution containing the potassium salt of N,N-diethylglycine or N,N-dimethylglycine. This selectively adsorbs hydrogen sulphide, carbon dioxide, small amounts of carbon disulphide, and hydrogen cyanide. The M solution, containing sodium alanine, adsorbs hydrogen sulphide and carbon dioxide simultaneously. The S solution, containing sodium phenolate, adsorbs carbon disulphide and mercaptans more effectively.

Claus sulphur recovery

A typical Claus sulphur recovery unit operates with "split" flow and three catalytic stages. Part of the acid gas is burnt with air in a furnace to produce sulphur dioxide and water vapour. Further hydrogen sulphide then reacts with the sulphur dioxide to produce water vapour and elemental sulphur.

Both reactions occur in the combustion stage and sulphur is condensed and removed from the exit gases. Further acid gas is added in a reheater and the mixture is passed to the first catalytic stage, containing a fixed bed of bauxite, where the second reaction continues. The reaction is equilibrium

Techniques for pollution control Waste Waste handling recovery of disposal

Noise

Installation issues

Closure

limited and overall conversion of hydrogen sulphide to sulphur depends upon the number of reacting and condensing stages. To achieve acceptable conversion three stages are required, or two stages and tail gas clean up.

Residual sulphur dioxide and hydrogen sulphide are passed to tail gas incineration before discharge to a vent.

Sulphur recovery plants should operate to a recovery efficiency of at least 99% during normal operation which will normally require three catalytic conversion stages with the final stage utilising a selective catalyst (eg Super-Claus Process) or with further treatment of the tail gas (where residual sulphur dioxide is reduced to hydrogen sulphide which can be recycled to the amine scrubbers.

Sulphur recovery units operate efficiently over a limited throughput range and operators should take this into account when designing their facilities. Further details on Claus plants are given in guidance on petroleum refining.

Liquid redox processes

A viable alternative to amine stripping followed by sulphur recovery in a Claus unit is direct sulphur recovery from weak hydrogen sulphide streams by liquid redox. Liquid redox technologies oxidise hydrogen sulphide in a liquid solution by the action of a number of mild oxidising agents to produce sulphur and water.

The Stretford process removes H2S from effluent gases. It is a continuous liquid purification system which converts H2S to elemental sulphur. The gas stream is first washed in an alkaline solution containing dissolved vanadates and anthraquinone disulphonic acids, fixing the hydrogen sulphide. The liquid from the washing stage then passes to a reaction tank, where virtually all the hydrogen sulphide is converted into elemental sulphur. The next stage, oxidation, separates the sulphur from the solution, which can then be returned to the washing stage. The sulphur is floated off as a froth for the final stage of recovery, when it can be recovered in a pure saleable form. The sulphur is usually recovered from the slurry in a molten form by decantation under pressure frequently with prior filtration and is obtained in a pure saleable form. The vanadium-based Stretford process can achieve removal efficiencies of 99.9%. The process is tolerant to fluctuating flowrates. However, the use of vanadium may have undesirable environmental implications. Other processes utilising non-toxic iron-based catalysts have been developed.

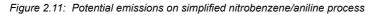
2.1.5 Organic compounds containing nitrogen

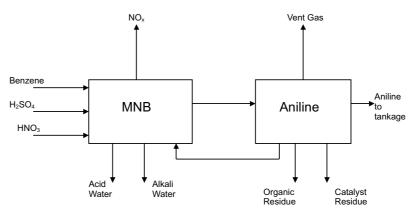
2.1.5.1 Aniline and Nitrobenzene

Aniline is produced commercially worldwide either by the reduction of nitrobenzene (the Bechamp process) or by the catalytic hydrogenation of nitrobenzene.

Catalytic hydrogenation can either be carried out in the gaseous or liquid phase and the gaseous route either uses a fixed bed or a fluidised bed catalytic reactor. The production of nitrobenzene and aniline are often integrated, as in the UK. The following description applies to the combined facility. A typical flowsheet is shown in Figure 2.11.

Introduction	1	Techniques for pollution control			Emissions			Impact		
In-process controls Emissions controls Ma		Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring		Installation issues





Benzene is converted to mono-nitrobenzene (MNB) in a mixture of nitric and sulphuric acids in a conventional stirred tank reactor at approximately 70 °C. Benzene is converted to MNB at a selectivity of around 97 percent. Effluent from the reactor is decanted into a separator where crude MNB is separated from the acid solution. This acid solution is concentrated by steam stripping and recycled back to the reactor. Crude MNB is washed, vaporised, and fed to a fluid bed reactor containing a copper-silica catalyst. Reactor effluent passes to a separator where two phases form. The organic phase contains water and is fractionated in a tower to retain aniline. The aqueous layer contains some aniline and typically is sent to the site wastewater system. The main wastewater sources are the crude nitrobenzene washwater and aniline water formed in the final separator.

Potential emissions to air:

- NO_X emissions from nitrobenzene are often controlled by caustic scrubbing prior to discharge to atmosphere.
- Vent gases (mainly methane and hydrogen) have a high calorific value and can be sent to the site fuel gas system or are burned in plant.

Potential emissions to water:

- Nitrobenzene has two liquid effluents; alkali water which represents a major pollutant, and acidic water. The acidic water stream is usually managed in a conventional bio-treatment plant after neutralisation.
- Alkali water (sometimes known as "red water") is particularly toxic and contains toxins such as nitrophenols and picrates. These toxins pass from the organic phase to the aqueous phase during washing. Typical concentrations range from 1,000 to 10,000ppm. Various abatement techniques have been employed including wet air oxidation, incineration and charcoal adsorption followed by incineration.

Potential solid waste streams:

· Catalyst residues (copper/silica) are either disposed of by landfill or recycled.

2.1.5.2 Derivatives of aniline

Cyclohexylamine

Cyclohexylamine is produced by the liquid phase hydrogenation of aniline in the presence of a catalyst such as cobalt, nickel or ruthenium/palladium. Aniline and hydrogen are reacted continuously and typical reactor conditions are 9 barg and 210°C, although high pressure processes (60 barg and 230°C) can also be used.

Introduction			Techniques for pollution control			Emissions			Impact		
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

Depending upon the end use of the cyclohexylamine, purification may not be necessary and is not required in the UK. Cyclohexylamine is usually stored under a nitrogen blanket.

Waste streams arising from cyclohexylamine production come from the reactor purge gases (feedstock hydrogen usually contains methane which must be removed periodically from the reactor) and from spent catalyst removal. Due to the high metals value of the catalyst reprocessing of spent catalyst is often carried out.

2.1.5.3 Methylamines

The three methylamines, monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) are all produced in equilibrium in the catalysed vapour phase alkylation reaction of ammonia with methanol, which is carried out at elevated temperature and pressure (see Figure 2.13).

The same basic process is used worldwide and consists of a fixed bed reactor followed by a distillation purification train. Variations occur in the catalyst type used and also in the distillation train arrangement with three main different configurations being used worldwide.

The product stream is distilled to separate the products from the ammonia. The initial column recovers ammonia that can be returned to bulk storage. The gaseous phase from the second column is returned to the reactor inlet. The bottom stream from this column is crude product and consists of MMA, DMA, TMA, unreacted methanol and water. This stream can be distilled into three product streams of MMA, DMA, DMA and TMA which can be sent to storage or to the secondary reaction circuit as required.

The methanol stream is purified and recycled to the reactor inlet. An aqueous stream with associated organic impurities for disposal is also generated.

Potential emissions to air:

- Process vents which contain methylamines should be routed via an absorption system in order to prevent emissions. Any adsorbed amines can then be recovered in a stripper and recycled within the process thus minimising losses.
- Due to the low odour threshold of MMA, DMA and TMA, it is important that leaks are minimised. This includes the design of storage and handling facilities, seals on pumps, and the minimisation of flanges in pipework.

Special control techniques include:

 emissions to air are minimised by scrubbing towers and adsorbers. If necessary to remove odour, back up systems may include biotreatment or incineration.

Potential emissions to water:

 Waste water generated in the reaction of methanol and ammonia plus scrubber water purges. All contain soluble amines and ammonia.

Special control techniques include:

- Minimisation of water usage in the scrubbing systems.
- Biological treatment of waste water.

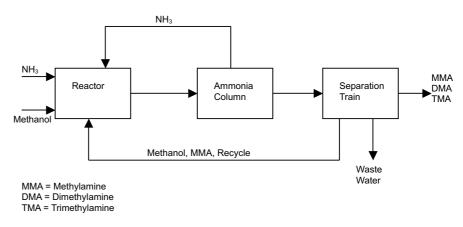
Potential solid waste streams:

Waste resulting from the periodic replacement of the catalyst in the reactors.

Figure 2.12: Manufacture of metha

Introduction	Techniques for pollution control			Emissions			Impact			
In-process controls Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

Figure 2.13: Manufacture of methylamines



2.1.5.4 Uses of methylamines

Aminoethanols

In the UK dimethylaminoethanol (DMAE) is produced commercially by the methylamination of ethylene oxide in the presence of a ruthenium catalyst at elevated temperature and pressure. By-products of the reaction result from the presence of trimethylamine impurities in the feedstock and from reactions between product DMAE and ethylene oxide to produce high molecular weight impurities.

In the reaction section an excess of dimethylamine is maintained in order to ensure the complete conversion of the ethylene oxide feedstock. The reaction is highly exothermic. A suitable reaction system consists of a loop reactor operated at a high recirculation rate and from which product can be continuously removed and fresh feedstocks and recycled dimethylamine continuously added. This system allows good control of temperature and of the rate of addition of the reactants both of which are critical to maintain high DMAE yield and minimise the formation of by-products.

The reaction product contains excess dimethylamine which is stripped out under reduced pressure, condensed and recycled to the reactor inlet. Temperature control of the stripper is required to prevent product DMAE being carried over in the overheads and being recycled to the reactor where it would react further to produce impurities. The crude product is vacuum distilled to separate light ends and DMAE from the heavy residues. The heavy residues contain DMAE, some of which is recoverable by further distillation before the residues are sent for disposal. The overheads DMAE stream is condensed before storage.

Vents from the reactor section, stripper unit and final distillation stage and other sources likely to contain dimethylamine may be collected together and vented via an acid scrubber. This generates a waste acid stream for disposal.

Dimethylcyclohexylamine

Dimethylcyclohexylamine (DMCHA) is produced commercially from the reaction between cyclohexanone, dimethylamine and hydrogen

There are two basic reaction steps involved in the production of DMCHA. The first involves the reaction between cyclohexanone and excess dimethylamine at elevated temperature and pressure to produce an imine. Any hydrogen present will react with cyclohexanone to produce cyclohexanol. The imine is then hydrogenated in the presence of a heavy metal catalyst at elevated temperature and pressure to give the product DMCHA. It is usual to carry out both stages of the reaction in a single agitated reactor.

Waste materials handling

Raw

Noise

Installation issues

Closure

Completion of the second stage of the reaction is indicated by a fall-off in hydrogen uptake. Excess hydrogen is normally flared and heavy metal catalyst is reclaimed by filtration of the crude reactor product.

The DMCHA is distilled off from the excess dimethylamine and water of reaction in a two stage system. Dimethylamine is removed in the overheads from the first column, condensed and returned to the reactor.

Vents from the condenser unit and other facilities on the plant will contain appreciable quantities of dimethylamine which must be removed prior to discharge to atmosphere.

The bottoms product is crudely separated in a phase separator producing an aqueous waste stream and then batch vacuum distilled. The water/light ends fraction is phase separated and the aqueous phase sent for disposal and the light ends recycled. Heavy ends residue will remain at the base of the column for subsequent disposal.

Minimisation of gaseous emissions from the plant is of great importance and all process vents and reliefs should be collected and scrubbed. This produces an amine contaminated aqueous effluent from the scrubber for recycle.

Dimethylformamide

Dimethylformamide (DMF) is produced by the highly exothermic reaction between dimethlylamine and carbon monoxide carried out in the liquid phase at elevated temperature and pressure in the presence of a sodium methoxide catalyst/solvent.

If a pure carbon monoxide feedstock is available then unreacted carbon monoxide and the excess dimethylamine present in the reactor off-gases can be separated from the product and catalyst system and recirculated back to the reactor inlet. At the end of the reaction, water is added to the reactor to deactivate the catalyst. The reactor product mix consists of the crude product and the catalyst/solvent. Various configurations of distillation/separation system are available all of which produce an unreacted dimethylamine stream which can be recycled, a product DMF stream and an aqueous waste stream. This can be treated by evaporative techniques to produce an aqueous phase and a solid waste stream for disposal.

A vent system collects all process vents and reliefs together and routes them to a flare system, if hydrogen is present, or to a suitable scrubbing system if the carbon monoxide feed is pure. In either method odorous dimethylamine emissions should be prevented.

The process is heavily fouling of heat transfer surfaces and regular cleaning is required which will generate significant quantities of aqueous effluent.

Dimethylacetamide

Dimethylacetamide (DMAC) is produced by the highly exothermic reaction between dimethylamine and methyl acetate carried out in the liquid phase at elevated temperature and pressure and in the presence of a sodium methoxide catalyst/solvent.

The production of DMAC is usually carried out in the same production facilities used for DMF. The basic difference is the quantity and composition of the effluent discharges. DMAC production leads to the production of more solid waste for disposal but in all other aspects the systems are similar.

Choline chloride

Choline chloride is manufactured by a two stage batch process involving hydrochlorination followed by ethoxylation of trimethylamine. The first step involves neutralization of trimethylamine with dilute hydrochloric acid to form a salt. This is carried out at atmospheric pressure and at a slightly elevated temperature (30-50°C).

In the second stage this salt is then ethoxylated using ethylene oxide to give choline chloride.

Management

Installation issues

Closure

There are two major side reactions which are liable to occur; ethylene oxide with water and ethylene oxide with hydrochloric acid unreacted from the neutralisation stage. These reactions produce monethylene glycol and ethylene chlorohydrin respectively.

Accidents

The acidic vapours resulting from the reaction section are routed to a scrubber before release to atmosphere.

The crude product can be purified by stripping under vacuum, separating the water associated with the hydrochloric acid feedstock from the choline chloride product. Contaminated water is removed as overheads and can be condensed and sent for disposal.

Quarternary ammonium salts

Quaternary ammonium salts have the general formula R4N+X- where X is typically a halide ion; R is an aliphatic or aromatic group. They are formed by the alkylation of amines. Amines react with an alkyl halide to form the next higher amine in the series and the reaction can proceed to the final stage to produce the quaternary salt.

In the UK trimethylamine (TMA) is reacted with dichloroethane (DCE) to produce the chlorinated quaternary salt as an aqueous solution. The process involves the batch reaction of the two liquid feeds, with the DCE present in excess, carried out at 2.5 barg. and 100°C. The reaction is exothermic and is controlled by carefully monitoring the addition of TMA and rate of heat removal. Upon completion of the reaction, water is added to form an aqueous product phase and a DCE organic phase. The DCE phase can be separated and recycled to the reactor whilst the remaining aqueous phase must be heated to generate the DCE/water azeotrope. This can be condensed and recycled. The pH of the aqueous product phase, stripped of volatile amine and DCE, is adjusted and the product stored.

Processes which use DCE are subject to EC Directive 90/415/EEC.

2.1.5.5 Ethylamines and isopropylamines

These are usually produced on the same plant on a campaign basis. The basic reactor system design is used worldwide with variations on the associated distillation system. Primary, secondary and tertiary ethylamines are produced concurrently but the formation of the tertiary isopropylamine is inhibited by steric effects. The manufacture of the various products is governed by the relative market demands and consequently the ability to recycle surplus product is required. Diethylamine is generally the most important product.

Ethylamines/isopropylamines are manufactured from the reaction between anhydrous ammonia and either ethanol or isopropanol. The reaction is carried out in the gas phase at elevated temperature and pressure in the presence of a hydrogenation catalyst eg. Raney-Nickel. Modern catalysts ensure essentially complete conversion of all the alcohol so that the requirement for azeotropic distillation and alcohol recovery columns, as installed on older plants, no longer exists. Hydrogen is usually recirculated via a condenser and gas separator to suppress the formation of reaction impurities and excess heat is removed to prevent degradation of the catalyst.

Ammonia is first removed as an overhead, recycled and then distilled to separate the mono-, di- and triethylamine streams from an aqueous waste stream. The aqueous phase will contain amines and these are reclaimed via a stripping column. Any inerts periodically purged from the system will also have associated amines present which are removed prior to discharge by an absorber/stripper system.

Periodic catalyst replacement, which is required as performance deteriorates, creates a solid waste catalyst stream which must be regenerated. As catalyst performance falls, heavy impurities are produced which are removed in the purification section and sent for disposal.

Noise

Installation issues

Closure

2.1.5.6 Ethanolamines

Ethanolamines are produced by the exothermic reaction between ethylene oxide and ammonia. All three derivatives; monoethanolamine (MELA), diethanolamine (DELA) and triethanolamine (TELA), are produced concurrently. The reaction is carried out at an elevated temperature and pressure, with ammonia in excess to ensure complete conversion of the ethylene oxide. The requirement for the presence of a catalyst is dependent upon the reactor operating conditions.

By-product residues are formed but are inhibited by the relatively slow reaction rates.

In response to changing market demands the relative distribution of MELA, DELA and TELA in the crude reactor product stream can be varied. A high ammonia to ethylene oxide ratio is used when MELA and DELA are required whereas recycling of product MELA and DELA is employed if DELA and TELA are the primary products. However, production of TELA also increases the production of heavy residues.

The crude product stream resulting from the reaction consists of water, excess ammonia, MELA, DELA, TELA and residues. This is separated by a series of distillation stages to provide product grade components and waste residues. Product TELA normally contains 15% DELA as an impurity. The excess ammonia and the water can be reclaimed and recycled to manufacture ammonia solution suitable for the reactor feedstock.

The initial purification step following the reactor involves the removal and recovery of the excess ammonia from the crude product stream. This is achieved by distillation. This ammonia is recycled in a recovery system in which the recovered ammonia is contacted with fresh anhydrous ammonia feed. Amines carried over in the recovery column overheads are usually recycled in this manner although the periodic purging of inerts from the system will tend to release ammonia and amines in small quantities.

Following removal of excess ammonia, the water must be removed from the crude product stream, generally by evaporation. Water/amines condensed overhead are used as a reflux to the system and as a feed to the ammonia scrubber. Purification of the mixed concentrated crude ethanolamines stream is carried out by vacuum distillation. Water which enters the purification system with the dehydration column bottoms is removed in the column overheads and must be condensed and purged from the system. Some loss of product is associated with this operation.

2.1.5.7 Acrylonitrile

A more detailed description of this process is available in the LVOC BREF(pp 267-289).

Acrylonitrile is produced by the vapour phase ammoxidation of propylene using excess ammonia in the presence of an air fluidised heavy metal catalyst. A fixed bed catalyst system may alternatively be used. Water, hydrogen cyanide, acetonitrile, carbon oxides and other organics (eg. acrolein) are formed as by-products. Catalyst efficiencies have increased to over 75%, reducing the quantity of by products passing to recovery or incineration.

The propylene is usually stored on site in either a brine cavity or storage sphere and ammonia either in refrigerated storage tanks at atmospheric pressure or under pressure at ambient temperature. Propane is usually present as a significant impurity of the propylene feedstock and must be purged from the system.

The reactor off-gases will contain catalyst fines and these are reclaimed, and returned to the reactor by either cyclones within the reactor or by external cyclones. Fresh catalyst must be continuously added to the reactor to replace losses. The reactor off-gases are quenched to remove the excess ammonia.

Emissions controls

Raw materials

Emissions Energy

Closure

Due to other impurities present at this stage the ammonia cannot be recycled and therefore dilute sulphuric acid is used as the quenching medium. The ammonium sulphate is treated and sold as a by-product.

Accidents

Noise

An alternative is to contact the reactor off-gases with a circulating stream of ammonium sulphate. In this system fresh sulphuric acid must be added to keep the system acidic and prevent the explosive polymerisation of both the acrylonitrile and the hydrogen cyanide. Catalyst is also removed in these process units and leaves the system with the ammonium sulphate liquor.

Ammonium sulphate can be removed from the liquor using a forced circulation evaporative crystallisation unit to produce a saleable by-product. A waste liquor stream from the crystallisation process is generated which contains some ammonium sulphate as well as organics removed in the quench process.

After quenching to remove the excess ammonia the reactor off-gases are normally scrubbed with chilled water. The vent gases from this unit contain mainly nitrogen but also some process materials. In most cases this vent gas is treated by incineration or flameless oxidation.

The absorber liquor is passed to a stripper where the product acrylonitrile and hydrogen cyanide are separated in the overheads from the acetonitrile.

The crude acetonitrile is stripped in a further column and is removed overhead whilst the heavy polymeric compounds present in the base liquors are separated out and concentrated. These heavy polymers are usually incinerated in the presence of a support fuel whilst the liquors can be partially recycled. The remainder of the liquor is treated with formaldehyde to remove any free cyanide prior to disposal. The acetonitrile can either be incinerated or purified further for sale.

The overheads from the recovery column, which consist of acrylonitrile and hydrogen cyanide, are distilled to produce the two products. Hydrogen cyanide is either sold (if a market is available) or incinerated. If hydrogen cyanide is stored on-site it is kept under acidic conditions and phosphoric acid, sulphur dioxide and acetic acid are often added to prevent polymerisation from occurring.

Release of acrylonitrile to atmosphere during storage can be significant and storage tanks must be vented to a safe location. In order to protect against possible polymerisation reactions occurring during storage small quantities of inhibitors are added. One of these, MEHQ (monoethyl ether of hydroquinone) requires small quantities of dissolved oxygen in order to be effective. Tank breathing losses must then be minimised by a suitable method, ie. an internal floating roof structure for storage tanks or connection to an incinerator. The high destruction temperature of acrylonitrile however may necessitate a support fuel - especially if the tank is nitrogen blanketed.

Potential emissions to air:

- Absorber vent gases containing mainly nitrogen but also some acrylonitrile, carbon oxides, unreacted oxygen and hydrogen cyanide.
- Various process vents.

Potential emissions to water:

Wastewater from wastewater stripping column treatment.

Special control techniques:

- Incineration or flameless oxidation of absorber off-gas and other process vents.
- Incineration with energy recovery or, preferably, use or sale of hydrogen cyanide co-product.
- Wet air oxidation of wastewater from the wastewater stripping column, followed by ammonium sulphate recovery.
- Powdered activated carbon treatment of acrylonitrile stripping and treated wastewater stripping column effluents

Emissions Management

controls

Raw

materials

Techniques for pollution control Waste Waste handling recovery of

disposal

Noise

Installation issues

Closure

2.1.5.8 Adiponitrile

In the UK, adiponitrile is produced by the electrohydrodimerisation of acrylonitrile. This is carried out in reactors which contain lead plated carbon steel electrodes which are periodically replaced as the product selectivity falls and the electrodes corrode. A fall in the selectivity is indicated by a change in the off-gas concentration, a higher voltage drop across the electrodes and the presence of more reaction by-products. At this stage the electrolyte must be removed to storage and the reactor water washed. These washwaters contain lead and must be carefully monitored and reprocessed. The spent electrodes are processed for steel recovery.

Accidents

The exit streams from the reactor consist of oxygen produced at the anode containing organics such as acrylonitrile, adiponitrile, propionitrile (formed by the hydrogenation of acrylonitrile), tricyanohexane (formed by the trimerisation of the acrylonitrile), and also hydrogen, iron and lead.

The reactor exit stream is routed via a two-stage separation system. The initial stage separates out the off-gases whilst the second stage is a gravity settler in which the electrolyte and organic phases are separated. The aqueous phase is fed to an extraction system and the organic phase is sent for adiponitrile recovery.

Off-gases from the separator pass to a scrubber, through which adiponitrile is recirculated, before discharge to atmosphere. This is important during start-up conditions when the system is saturated with acrylonitrile.

In the adiponitrile recovery section unreacted acrylonitrile is recovered and fed back to the extraction stage. This will also contain some of the electrolyte and any other additives. In addition the propionitrile can be recovered and either used as a raw material, sold or sent for disposal. It has a high calorific value and may be suitable as a support fuel for incineration. An adiponitrile stream is produced which requires further purification.

The adiponitrile is vacuum distilled to produce an adiponitrile product stream and high and low boiling fractions which include the trimers of acrylonitrile which are suitable for incineration. Vacuum exhausts from each of the columns are scrubbed with chilled adiponitrile.

Recovered streams from the separator unit and the acrylonitrile recovery stage are fed into an extraction unit in which the adiponitrile and additives can be recovered and recycled to the reactor inlet. Iron, lead and electrolyte remain in the aqueous phase.

A crystalliser is used to reclaim the majority of the phosphate and borate species from the electrolyte.

The aqueous phase from the crystalliser is sent for lead removal in which sodium hydrogen sulphate is added to form a lead sludge which can be separated by centrifuge. The aqueous wastestream after this operation must be carefully monitored for lead levels and further downstream treatment is required to reduce lead to acceptable levels. This however, will produce a solid waste containing lead for disposal.

2.1.5.9 Hexamethylene diamine

Hexamethylene diamine (HMD) is currently produced by the catalytic hydrogenation of adiponitrile. The process is available as either a high pressure process or a low pressure process.

In the high pressure process liquid ammonia is used to suppress the formation of by-products and with typical hydrogenation temperatures of 80 to 150°C, this results in operating pressures in the range 200 to 340 barg. to maintain the ammonia in the liquid phase.

Management

Raw materials

Closure

Noise

Installation issues

In the low pressure process alcohols and/or an aqueous alkali are used to suppress the formation of by-products and this allows a lower operating pressure.

The hydrogenation catalyst used for the reaction can either take the form of a catalyst slurry or a fixed bed. Patented catalysts used include reduced cobalt, iron, ruthenium or Raney-Nickel.

Impurities in the adiponitrile feedstock are hydrogenated and tend to form low boiling impurities in the reactor system. Several by-products are also formed including hexamethyleneimine (HMI), bis-hexamethylene triamine (HMT) and 1-2 diaminocyclohexane (DACH). One by-product only formed in the low pressure process is 2-aminomethylcyclo-pentylamine (AMC) produced by the caustic catalysed re-arrangement of adiponitrile.

Low pressure process

The basic raw materials for this process are adiponitrile, sodium hydroxide, hydrogen and the Raney-Nickel catalyst (stored under water). Hydrogen is used in excess in the reaction which is carried out at pressures around 35 barg. and at temperatures below 100°C. The reactor is a gas-lift design. The reaction mass consists of two liquid phases and a solid phase. The major liquid phase is the crude HMD product whilst the solid phase is the Raney-Nickel catalyst. The minor liquid phase consists of concentrated caustic.

Crude product is decanted from the separation vessel and the clarified HMD product continuously separated from the solid phase and the concentrated caustic phase. Both these latter phases are returned to the reactor whilst the product phase is fed through hydrocyclones to remove entrained catalyst before refining. Catalyst is continuously removed from the reactor, washed and a portion returned to the reactor along with fresh catalyst. The remainder can be sold into the metals recovery industry.

In the refining section the crude HMD is distilled to remove low and high boiling point impurities and water. A series of distillations generates a low boiling fraction, pure HMD and a high boiling HMD which can be further batch distilled under vacuum to recover HMD before disposal of the residues. Water recovered in the refining stage contains some HMD and imines which can be recycled to the reactor via the catalyst washing stage. Both the high and low boilers have no commercial value and are usually incinerated, with energy recovery.

High pressure process

The basic raw materials for this process are adiponitrile, liquid ammonia, hydrogen and an iron catalyst. The ammonia is used in excess and over 80% of the ammonia is recycled.

A 2-stage trickle bed reactor system is used for the reaction and contains the fixed bed catalyst. The fully reduced iron catalyst, which is pyrophoric and has a limited service life, requires regeneration in a hydrogen atmosphere.

Reactor temperature control and the age of the catalyst are critical to the formation of by-products. If the temperature is too high, the formation of the hexamethyleneimine is favoured whilst if the temperature is too low the formation of aminocapronitrile is encouraged. As the catalyst ages the production rate of HMD falls.

The reactor product passes to a separator which operates at 180°C and 250 barg. The liquid product is removed from the base of the unit and let down to 40 barg. The off-gases pass through a secondary cooler to a secondary product separator where again the liquid bottoms are removed and let down to 40 barg. The off gases from both units are recycled to the first reactor. The liquid phase is sent to a let-down vessel where the pressure is reduced and dissolved gases are released and separated.

These gases, mainly hydrogen and methane, pass through a condenser where ammonia is removed before being sent through an absorber to recover any remaining ammonia and then a water scrubber before being used as a fuel gas.

Management

Raw

Noise

Closure

The liquid from the let-down vessel contains ammonia and this is boiled off in an ammonia reboiler/still, condensed and recycled. The crude HMD from the bottom of this still is cooled and stored in a nitrogen blanketed storage vessel. Vent gases from this stage are routed to the ammonia recovery system. In this storage facility, water is added to the crude HMD and forms an azeotrope with the hexamethyleneimine impurity to facilitate its later removal by distillation.

Vacuum distillation is used to reduce impurities in the HMD to the low levels required, typically less than 20 ppm. The water/imine azeotrope fraction is removed along with light and heavy fractions both of which contain significant quantities of HMD and are therefore processed further in a batch still. The light and heavy fractions can both be re-used. The light fractions can be sold and the heavy fractions can be used in any upstream adiponitrile plant by recycling to the adiponitrile purification process.

Purified HMD is mixed with water to prevent solidification of the pure form which occurs at temperatures below 45°C. Storage tanks are nitrogen blanketed to prevent product oxidation and discolouration.

Air leaks into columns operating under vacuum cause the formation of impurities. To prevent this, carbon dioxide is routinely added at the top of distillation columns.

2.1.5.10 Acrylamide

Acrylamide is manufactured by the reaction between acrylonitrile and water in the presence of a copper based catalyst to produce an aqueous solution of the product. Unreacted acrylonitrile can be recycled within the process to give almost complete chemical conversion.

Acrylonitrile and deaerated water are fed into a continuous stirred tank reactor operating at 100°C and 4 barg, together with a catalyst stream. The demineralised water feed can come from scrubbing plant, vacuum pumps and water flushed seals. By this method any product or acrylonitrile losses are recycled to the reactor system and overall losses can be minimised.

The catalyst carry over in the reactor exit stream is removed by filtration before passing to a purification system. Acrylonitrile and product can then be reclaimed from this slurry by steam stripping and returned to the process whilst the remaining effluent slurry consisting of water, filter precoat and copper catalyst are sent for disposal.

The purification system consists of a vacuum distillation column followed by a wiped film evaporator. Unreacted acrylonitrile and water are removed overhead and condensed by water cooled and refrigerated condensers before being recycled back to the reactor. The product stream is a 50%w/w aqueous solution of acrylamide.

Off-gases from the condenser system, which pass to the vacuum system, will contain acrylonitrile and these are scrubbed to reclaim the acrylonitrile. The water used to irrigate these scrubbers can be used as the primary feed water to the reactor.

The 50%w/w aqueous solution of acrylamide can be further purified by passing through an activated carbon adsorption column followed by an ion exchange column to remove cations (mainly copper). The spent carbon is disposed of periodically. Any copper passing through the screening filters renders the carbon unsuitable for regeneration. The ion exchange columns are periodically regenerated with acid. This acid stream is neutralised with caustic soda solution to precipitate copper hydroxide which can be filtered and disposed of. The filtrate, containing some acrylamide and copper, must also be sent for disposal.

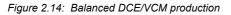
Introductio	Introduction			Techniques for pollution control			Emissions			Impact		
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

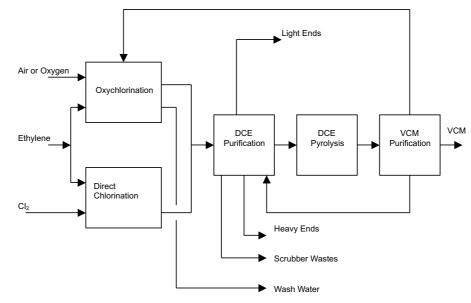
2.1.6 Organic compounds containing halogens

2.1.6.1 Dichloroethane and vinyl chloride

This process is described in more detail in the LVOC BREF (pp 291-322).

The manufacture of vinyl chloride monomer (VCM) is the largest use of 1,2 dichloroethane (DCE) and the processes are often integrated. The "balanced process", shown in Fig. 2.14, includes the formation of the intermediate DCE from ethylene and chlorine by direct chlorination and oxychlorination of ethylene with recycle HCI, followed by thermal cracking to form VCM.





DCE is manufactured primarily by the direct chlorination of ethylene generally in the liquid phase. The reaction is catalysed by metal chlorides including ferric, aluminium, copper and antimony chlorides and substitution reactions are inhibited by oxygen.

The process can be operated at high or low temperatures. The latter produces less by-products and allows the use of lower grade construction materials, whilst the former produces DCE in the gaseous form and so the catalyst does not have to be removed by washing. The low temperature (less than 100°C) route is the more common in Europe.

Hydrogen chloride generated in the cracking of DCE to VCM is reacted in the gas phase in either a fixed bed or fluidised bed oxychlorination reactor containing a copper chloride catalyst with ethylene and either oxygen or air to produce more DCE. In the latter case, air and ethylene are fed in slight excess of stoichiometric requirements to ensure high conversion of hydrogen chloride, however significant quantities of chlorinated by-products are formed. Use of oxygen in place of air requires a larger excess of ethylene in the feed and permits lower temperature operation. It gives improved product yield with significantly reduced by-products and lower volume of vented gases. The reaction temperature is up to 350°C and at a pressure up to 130 barg.

DCE must be purified before cracking. The first purification stage consists of scrubbing the product stream with water and then with caustic solution to remove entrained catalyst and some water-soluble organic compounds. Water and low boiling point organics produced in the oxychlorination reactor, and recycled DCE from the thermal cracking process, are removed as overhead in a light-ends distillation

column, the organic components being transferred to storage prior to destruction or further processing and sale. Pure, dry DCE is taken overhead from a second distillation column and residual tars are stored prior to further fractionation, processing, or destruction with some or all of the light ends.

DCE is converted to VCM with the release of HCl by thermal cracking. Following quenching, hydrogen chloride is removed by distillation in which ethylene and acetylene are also evolved; these can be hydrogenated before being routed to the oxychlorination reactor. VCM is taken overhead from a second distillation column from which the remaining crude DCE, containing most of the impurities, is routed back to the DCE purification process. Liquid vinyl chloride is scrubbed to remove HCl before transfer to a pressurised storage vessel.

Potential emissions to air:

- Fugitive emissions of chlorinated hydrocarbons from valves, flanges, and other minor sources.
- Chlorinated hydrocarbons from storage of raw materials, intermediates, and products.
- Chlorinated hydrocarbons from reactors and columns, vacuum pumps, sampling systems, and wastewater collection and treatment systems

Special control techniques include:

- High integrity mechanical equipment: double seals on pump shafts, bellow seals or similar on valves, high quality flange gaskets.
- Incineration of all vents with chlorinated hydrocarbons, including those from safety valves, with recovery of HCI.
- · Closed sewers.

Potential emissions to water:

- · Significant organic effluent from the DCE purification section.
- Catalyst from reactors, particularly copper from fluid bed catalyst oxychlorination units.
- · Cleaning water, seal water, aqueous phase from tankage.
- Inorganic salts from water demineralisation.

Special control techniques include:

- Stripping of chlorinated hydrocarbons with air or steam, and returning to the process.
- Removal of copper by alkaline precipitation at pH 11-12, or by electrolysis; copper catalyst in the effluent is thought to increase the possibility of dioxin emissions to aquatic media.
- Alkaline treatment of non-volatile organics such as choral to allow stripping or degradation.

Potential solid waste streams:

- emissions of lights and heavies from the DCE purification system if not used or destroyed.
- Spent lime from VCM final purification.
- Spent catalyst from reactors.
- Sludge from settling ponds.
- Cracker decoking waste.

Special control techniques include:

• High temperature incineration of those chlorinated by-product streams that cannot be used beneficially, with scrubbing of incinerator waste gases.

Storage of vinyl chloride

VCM is stored as a liquid under pressure in spheres or tanks. PVC manufacturing plants remote from VCM production sites receive deliveries of liquid VCM by road or rail tankers, or ship, which are normally unloaded by displacement. Storage vessels and loading lines may be vented to a monomer recovery system, and may be blanketed with an inert gas such as nitrogen. An inhibitor is often added to the vinyl chloride during storage and transport to prevent polymerisation.

Potential release routes to air

Introduction	Techniques f	Techniques for pollution control			Emissions			Impact			
In-process controls Emissions Manag	ement Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues		

• Vents from monomer recovery and blanketing systems, which could be routed to a vents incinerator. There should be no significant emissions to water and land.

2.1.6.2 Other halogenated hydrocarbons

General halogenation reactions are covered in the IPPC Guidance Note on Speciality Organic Chemicals as most are batch processes. In large scale plants an organic feedstock is reacted with halogen or halide in a pressurised continuous reactor at elevated temperature in the presence of a catalyst. A range of halogenated organic products is formed which are separated by condensation and distillation in a train of columns depending on the complexity of the mixture. Unwanted by-products are recycled to the process where possible. Unreacted halogen and halide should be recovered and returned to the process or other productive use wherever practicable. Where it is necessary to vent a gas stream, emissions of halogenated hydrocarbons and other VOC's should be minimised by the techniques detailed in section 3. Emergency vents should be directed to a collection system with suitable abatement facilities.

Examples of these processes include the reaction of ethylene and chlorine to form 1,2 dichloroethane (DCE) and its subsequent conversion to vinyl chloride which is described in section 2.1.5.1 DCE can be further chlorinated in the presence of oxygen to trichloroethylene and perchloroethylene. The hydrochlorination of methanol yields methyl chloride which can be further chlorinated to methylene chloride.

Hydrochlorofluorocarbons are made by the hydrofluorination of chlorocarbons such as chloroform. By-products include some hydrofluorocarbons which have high global warming and ozone depletion potentials. In the absence of productive use, they should be incinerated with scrubbing of the resulting gases and not released to the environment. Residues such as heavy ends from distillations should be incinerated and not released to land.

2.1.7 Polymers

2.1.7.1 Polyvinyl chloride (PVC)

PVC resins can be produced from vinyl chloride by four manufacturing processes: suspension, emulsion (dispersion), bulk (mass) and solution.

In the UK, homopolymer resins are produced only by the suspension and emulsion processes.

Suspension polymerisation

The suspension process comprises of the batch polymerisation of vinyl chloride under pressure in demineralised water with vigorous agitation; followed by the stripping of residual vinyl chloride from the polymer resin slurry, monomer recovery and recycling within the manufacturing process, and by the drying and screening of dewatered resin, and subsequent storage of PVC.

disposal

Closure

The reactor vessel is first evacuated to remove oxygen, which inhibits the reaction, then charged with raw materials. The batch is heated to reaction temperature by external heating. Thereafter the temperature of the exothermic reaction is regulated by cooling water, to produce resin grades of particular molecular weight. Agitation and suspension stabilisers control the size of the product. Polymerisation is stopped when the required conversion is reached.

Unreacted VCM, present in the water, polymer resin and vapour space above the polymer, is removed batchwise either in the reactor vessel, a separate holding tank, or in a stripping column by steam stripping under vacuum. It is then transferred to a monomer recovery system for separation from water and inert gases, prior to being recycled to the process.

The stripped PVC slurry is passed through a centrifuge to remove most of the water before the resin is dried in a rotary or fluidised bed dryer. This may be preceded by flash drying. After drying, the resin is screened to remove oversized particles and transferred to storage silos before being bagged or transported off-site in tankers.

Potential emissions to air:

- VCM from reactors, monomer recovery, and PVC stripping and drying.
- PVC particulate matter from transfer and storage
- VCM from wastewater collection and treatment.

Special control techniques include:

- Reduction of reactor opening frequency by use of anti-fouling agents and internal spray systems; displacement of reactor gas before opening.
- Recovery of VCM from gas streams by carbon adsorption, refrigerated condensation, absorption/ desorption with solvents, membranes or other techniques.
- High integrity mechanical equipment for VCM duties
- Fabric filters to abate dust from driers and other sources.

Potential emissions to water:

- Salts from water demineralisation.
- VCM and surfactants in reactor water, washwater, sealwater.
- PVC in reactor water.

Special control techniques include:

- Stripping of VCM from wastewater by air or steam; incineration or other treatment of stripped VCM.
- Settling of PVC dust, possibly chemically aided.
- Re-use of treated water for process washing.

Potential solid waste streams:

Waste PVC which may contain residual VCM.

Emulsion polymerisation

Emulsion polymerisation produces resins with a smaller particle size and lower porosity than the suspension method and is carried out in water using emulsifiers and surfactants. The VCM is dispersed in the water by agitation. All the VCM can be charged initially or it can be added in stages to produce resins with a range of properties and different particle sizes needed for particular applications. During the polymerisation process, a portion of the PVC forms large agglomerates or `pebbles' up to 1cm in diameter. These will be disposed of as a solid waste containing a significant amount of entrained vinyl chloride.

After polymerisation, unconverted VCM (up to 15%) is removed from the latex by vacuum and steam stripping and transferred to the monomer recovery system. Following the stripping operation the pebbles are removed before the latex is spray dried. The PVC is then screened to remove oversized

Introduc	ion		Techniques for	pollution control		Emissions			Impact		
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

particles, and is often passed through a milling operation before storage. An alternative route is to coagulate the PVC particles and separate them from the water by centrifuging or filtration and then dry using a similar system as for the suspension polymerisation route.

Potential emissions to air:

- VCM from reactors, monomer recovery, and PVC stripping and drying.
- Particulate matter from transfer and storage of PVC.
- VCM from wastewater collection and treatment.

Special control techniques include:

- Reduction of reactor opening frequency by use of anti-fouling agents or lined reactors, though this is technically harder than for suspension PVC, plus purging before opening.
- Stripping in reactor or, preferably, in an external thin film stripper.
- Incineration of vents containing VCM.

Potential emissions to water:

- PVC, surfactants and VCM from process wastewater.
- · Inorganic salts from water demineralisation.

Special control techniques include:

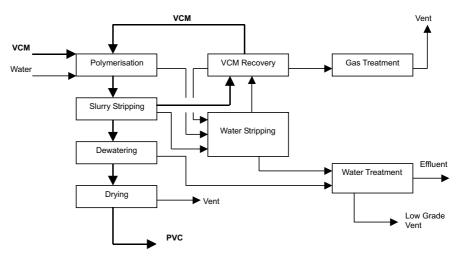
- Collection of stripper condensate, VCM recovery condensate, wash water and seal water for treatment in a water stripper.
- Removal of very fine PVC particles by coagulation techniques.

Potential solid waste streams:

- Residual VCM associated with waste PVC
- Polymer from reactor cleaning operations.

The properties of PVC can be modified by co-polymerising the VCM with a wide range of other monomers of which only a few, such as vinyl acetate and the olefins, are of commercial importance. Co- and ter- polymers are manufactured in similar processes to those used for the homopolymer. The emissions from these processes will be similar.

Figure 2.15: PVC production: suspension



Emissions controls

Management

Techniques for pollution control Raw Waste materials handling

te Waste dling disposal Emissions Energy

Noise

Installation issues

Closure

2.1.7.2 Polystyrene

Three grades of polystyrene are produced in the UK; crystal (general purpose), high impact (HIPS) and expandable polystyrene (EPS).

Accidents

General purpose and high impact polystyrene

Polystyrene is continuously produced by either the mass process or the solution process. The mass process uses no water or organic solvent whereas the solution process uses a solvent, typically ethylbenzene. The solution process is the significant process in the UK and is described below.

Styrene is steam stripped of inhibitors and blended with plasticisers and ethylbenzene and fed through a series of agitated reactors under vacuum. Initiation of the polymerisation is by heat or the addition of catalysts. After polymerisation the reactor product is passed through two devolatisation vessels under vacuum to remove the ethylbenzene and styrene for recycling. Water is injected into the second vessel to cause foaming and then decanted from the product.

The polystyrene is pelletised in an extruder, dried and then stored.

HIPS is produced by a batch polymerisation process similar to the process for producing general purpose polystyrene. However, HIPS has its physical properties modified by the addition of granulated rubber to styrene in the reactor with mineral oil and inhibitor. Polymerisation takes place in the reactor with reflux under vacuum. The polymer mixture undergoes devolatilisation and pelletisation using an identical process to that used for crystal polymerisation.

Potential emissions to air:

- Styrene, toluene, EB from storage, tanker unloading and filling, vessel filling.
- Styrene, EB from vacuum pumps and devolatilisation systems.
- Particulate matter from product drying and handling.

Potential emissions to water:

- Styrene monomer in effluent from devolatilisation systems.
- Decanter effluent.

Potential solid waste streams:

- Polystyrene residue from the separator following devolatilisation systems
- Solid residue from separator.

Expandable polystyrene

Expandable polystyrene (EPS) is produced as small, white, spherical beads with a diameter of about 1mm. Two main grades are produced, one suitable for food packaging, and the other (containing brominated compounds) which has flame retardant properties for use as insulation. The beads contain pentane to provide expansion properties when moulded by customers.

The suspension process is used, with batch polymerisation of styrene suspended in water. It comprises polymerisation, dewatering, drying, sieving and coating. Polymerisation is carried out in a stirred tank reactor which is heated and cooled at the appropriate part of the cycle. Styrene, catalysts, suspension stabilising agents, buffer agents and flame retardant are added to the reactor initially and later pentane, after which the reactor is heated to 130°C. The suspension stabilising agent is either bentonite and gelatine or calcium phosphate.

The polystyrene slurry is sieved and then centrifuged to separate the beads. The waste water contains some beads, suspension stabilising agents, traces of spent catalyst and the buffer agents and passes through a series of settling tanks to remove the solids prior to disposal. The collected waste solids may be sold or disposed of to landfill. The beads are next coated with an anti-static agent and dried in a flash dryer followed by a fluidised bed dryer. The drier air is cleaned in bag filters before discharge to atmosphere. The collected solids may be sold as low-grade product.

Introduction	1		Techniques for	pollution control		Emissions			Impact		
In-process controls	In-process Emissions Management		Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

After the fluidised bed dryers, the beads are sieved into various size ranges and collected in hoppers purged with air direct to atmosphere, to prevent creation of a flammable mixture with pentane.

Potential emissions to air:

- Pentane and styrene from storage.
- · Pentane from filling and opening the reactor and buffer vessel.
- Styrene during polymerisation in the reactor.
- Pentane from the dryers and product hopper.
- Particulate matter from product drying and handling.

Potential emissions to water:

Decanter effluent.

Potential solid waste streams:

Solid residue from separator.

2.1.7.3 Polymerisation of acrylates

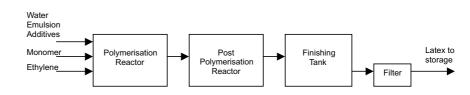
Acrylic acid esters (methyl to 2-ethylhexyl) are clear, colourless liquids with strong acrid odours; multi-functional speciality acrylates are more viscous. Acrylate monomers undergo vinyl-type emulsion polymerisation in water or solvents. Processes used to produce acrylate polymer compounds, or acrylate solution polymers, are very similar differing only in size of operation and additives used. Most reaction systems are batch but there are some continuous ones.

Water-based acrylic emulsion polymers

The acrylate monomers and other monomers such as styrene, vinyl acetate, acrylamide, methacrylamide, acrylic and methacrylic acid, and acrylonitrile are charged either to a pre-mix vessel or directly to a reactor where they are mixed with water stabilisers and additives. Where a pre-mix vessel is used the reactor is normally equipped with some form of heating. Either a closed or refluxed reactor is normally used. Some reactors vent to caustic scrubbers, generating a wastewater stream containing spent caustic and sodium acrylate.

Following polymerisation the material is filtered and sent to storage. Sometimes an intermediate vessel is used before filtration for balancing, additions or dilution. Surfactants may be used to prevent coagulation and subsequent blocking of the filters.

Figure 2.16: Simplified emulsion polymerisation process



Potential emissions to air:

· Monomers from pre-blend tanks, reactor charging, reactor operation, storage tanks and drum filling.

Special control techniques include:

Incineration of VOC streams from storage tanks and process vessels.

Potential emissions to water:

 Monomers, acrylate polymers, surfactants from reactor washdowns and process water, filter washings.

Introduction			Techniques for	pollution control		Emissions			Impact		
controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

- Spent caustic solution containing acrylates, sodium acrylates from scrubber.
- Special control techniques include:
- Waste water recycling

Potential solid waste streams:

- S²Off-spec polymer, often reworked.
- · Polymerised solids from reactor fouling
- Polymer residues from filters.

Solvent based acrylic polymers

The solvent-based process is a batch process similar to that for water based emulsion polymers. The acrylate and other monomers are pre-mixed with stabilisers and additives, and fed slowly into a reactor containing solvent which can be heated or cooled. Commonly used solvents include xylene and toluene. The vessel is typically fitted with a water-cooled condenser venting to atmosphere. The product is filtered before being transferred into drums. Sometimes an intermediate vessel is used before filtration for balancing, additions or dilution. For some products, the solvent may be stripped-off, using vacuum stripping, and recycled back to the process.

Typically, the vessels will only be washed out between batches using different solvents. The vessel is first rinsed with solvent, which is reclaimed by distillation, and then boiled out with caustic, the spent caustic being discharged into the plant wastewater system.

Potential emissions to air:

 Monomer and solvent from the preblend tank, reactor charging, reactor operation and washdown and storage tanks.

Potential emissions to water:

- Monomers, acrylate polymers, surfactants from reactor washdown, process water, filter washings.
- Spent caustic solution containing acrylates, sodium acrylate from scrubber.
- Spent caustic from reactor washdown.
- · Solvents.

Potential solid waste streams:

- Polymerised solids from reactor fouling.
- Polymer residues containing solvent from filters.

Acrylic moulding powders

Acrylic moulding powders are produced using emulsion and suspension polymerisation techniques. The process involves batch polymerisation of methyl methacrylate with other co-monomers that are mixed in a preparation vessel prior to being charged to an autoclave.

The autoclave has provisions for both heating and cooling and a typical charge consists of deionised water, polymethacrylic acid, phosphate buffer and other minor additives. Polymerisation is initiated by heating. The exothermic reaction is moderated by controlled cooling of the vessel. Overpressure may be caused by loss of stirring or cooling. Gases from the autoclave are removed via a vacuum system which discharges to atmosphere.

After polymerisation the product is sieved and stored as a slurry. The slurry is centrifuged to remove water and unreacted organics, and then re-slurried with water. This slurry is dewatered and dried in a second series of centrifuges which discharge the product to a rotary steam-heated dryer. The product is cooled, sieved and packed or routed to storage bins.

Potential emissions to air:

- · Methyl methacrylate, acrylates from storage, preblend vessel, autoclave, and vacuum system.
- Particulate, acrylate monomers from driers, filters.

Introduction	1		Techniques for	pollution control		Emissions			Impact			
In-process controls	In-process Emissions Management		Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

· Particulate matter from product storage hoppers.

Potential emissions to water:

- Acrylate monomers and polymer from autoclave washwater, slurry wash water.
- · Acrylate monomers and phosphates from centrifuges.
- Water seal containing acrylate monomer from liquid ring vacuum pump.
- · Warm wash water containing monomer and polymer from vessel cleaning after each campaign.

Potential solid waste streams:

- · Polymer fouling from autoclaves.
- Polymer from centrifuges, settling tanks.
- Polymer, dust from filter residues.

Poly methyl methacrylate

Poly methyl methacrylate (PMM) is produced from methyl methacrylate in a batch process. PMM is generally combined with additives which are typically colourings such as inorganic compounds of iron, titanium and cadmium.

The monomer is heated and charged to the reactor. Catalyst is added and, once the syrup has reacted sufficiently, air pressure is used to transfer the hot monomer/polymer mixture via a cooler to the stirred blending vessel. Here colouring agents are added. Lines are back-flushed with monomer to prevent build-up.

The mixture is transferred to an evacuator vessel where vacuum is drawn to remove entrained gas bubbles, before being transferred, via a filter, into the casting chamber. Here PMM sheets are cast between glass plates sealed with a flexible gasket and placed in the polymerisation oven. The PMM is heat-treated to achieve polymerisation. Both the glass plates and PMM sheets are rinsed using treated de-mineralised water and detergents. Wash water goes to the wastewater collection system. The PMM is air dried, inspected for imperfections then wrapped in polythene and stored. Vessel washing residues are sent for recovery.

Potential emissions to air:

Methyl methacrylate from storage, vessel filling, blender, evacuator and vacuum pump.

Potential emissions to water:

- Waste water from heating, cooling, washing, rinsing operation (pH, sodium based corrosion inhibitor, biocides).
- Acid and caustic from water demineralisation operation.
- Seal fluid from vacuum pumps.

Potential solid waste streams:

- Particulate matter (dust) from cutting, trimming of sheets.
- Methyl methacrylate and PMM from overmake, drips and spills.

2.1.7.4 Nylon

Nylon salt

Nylon salt is the precursor for nylon polymers. It is produced by mixing the two monomers hexamethylene diamine (HMD) and adipic acid together in an aqueous solution in a stoichiometric ratio. The resultant product is an aqueous solution of the nylon salt of approximately 50% w/w concentration.

A saturated aqueous solution of adipic acid is fed into a dissolver unit, and demineralised water and half the required HMD is added. The reaction is instantaneous and slightly exothermic.

The product is transferred to the first reactor vessel where the majority of the remainder of the HMD required for neutralisation is added. The reactor is operated under vacuum and the heat of reaction is removed by water evaporation. This water contains some HMD and is condensed and recycled back to the reactor.

The nylon salt from the first reactor is transferred to a second reactor, also operating under vacuum, where small quantities of HMD are added under pH control. The resultant nylon salt is then pumped to storage where either HMD or adipic acid is added as necessary to adjust the pH to the desired level. This determines the adipic:HMD ratio and hence the eventual nylon polymer molecular weight.

A filtration step is often required to remove solid impurities (usually iron corrosion products) from the salt solution.

Storage of nylon salt is carried out under a nitrogen blanket to prevent discolouration of the product by air oxidation. Stabilisers such as hydrazine are also added to improve the stability of the salt and prevent colour degradation.

Potential emissions to air:

Vents from feed stock vessels.

Potential emissions to water:

Filter washings.

Potential solid waste streams:

Filter aid and cake.

Nylon polymers

Nylon polymers are produced by polymerising nylon salt. The properties of the nylon polymer can be modified to suit end use requirements by the addition of small amounts (ppm levels) of various additives such as copper acetate, potassium iodide, borax, Topanol, sodium hydrogen phosphite, copper bromide etc. Titanium dioxide is often added (less than 2% w/w) as a whitener to fibre grades and caprolactam can be added (3-9% w/w) to make a co-polymer.

A typical production process involves the following basic steps which are common to all nylon polymerisation processes, although some variations do occur depending upon the end use of the nylon polymer.

Nylon salt solution is heated and transferred to a measuring vessel where additives are fed in. This mix is then evaporated to increase the salt strength. The off-gases which contain trace quantities of HMD are condensed and disposed of. After completion of the evaporation cycle the mix is transferred to an autoclave unit.

If caprolactam is to be added it is done so at this stage before polymerisation occurs. Polymerisation processes have a range of process cycles, but essentially involve applying heat to typically 300°C at elevated pressures (typically 18 barg.) to remove the remaining water content of the nylon salt as well as the water of reaction generated by the polymerisation reactions. The water driven off generates a waste stream. Air is excluded to prevent oxidation of the polymer.

At the completion of the polymerisation reaction when the properties of the mix are acceptable, the molten polymer is extruded from the autoclave through a die. Depending upon whether the final product (e.g. fibre) is being produced directly or whether nylon chips are being produced as an intermediate stage the hole size of the die is varied. In the latter case strands several millimetres in diameter are extruded and chopped into chips which can then be easily handled and transported to any subsequent spinning or moulding stage.

Off specification product produced in the manufacturing process can usually be blended into lower grade products with less critical specifications thus minimising the generation of a solid waste.

Introduction	Techniques for	pollution control		Emissions			Impact			
In-process controls Emissions controls Ma	 Raw materials		Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues	

Potential emissions to air:

- Feed stock vapours from storage.
- Off-gases from the evaporator and condensers in the polymerisation section.
- Off-gases from the die cleaning scrubber.

Potential emissions to water:

- Waste streams from the condenser systems
- · Waste streams from the scrubber system.

Potential solid waste streams:

Off specification product.

2.1.7.5 Acrylic fibres

Acrylic fibres, which consist of polyacrylonitrile (PAN), can be produced either by the heterogeneous polymerisation of acrylonitrile in solution or by solution polymerisation. The latter process allows the acrylic fibre to be spun directly from the polymer solution whilst the former requires the separation and drying of the solid polymer before it is redissolved prior to spinning and is therefore a more energy intensive process.

Two principal spinning processes are used. In dry spinning an organic solvent such as dimethylformamide, which has a low volatility and can therefore be easily recovered, is used to dissolve the PAN. The solution is forced through a spinneret and the solvent evaporated using hot air and the strands allowed to form. In wet spinning the PAN fibres emerge from the spinneret into a water bath. The fibres coagulate and the solvent diffuses into the water. A solvent recovery plant is required to recover the solvent.

Commercial PAN contains various additives designed to modify its properties and also minor amounts of unreacted acrylonitrile. These additives can include neutral monomers such as methyl acrylate, methyl methacrylate and vinyl acetate to copolymerise with the acrylonitrile and increase the stability of the polymer in various solvents. Other additives include ionic monomers, halogen containing monomers and compounds such as sodium styrene sulphonate which provides dyesites enhancing dyeability.

The choice of process is largely determined by the end use of the fibres. Acrylonitrile is moderately water soluble but the polymer is insoluble in both acrylonitrile and water. This makes aqueous heterogeneous polymerisation, either batchwise or continuous, a natural choice where the PAN polymer is to be isolated prior to redissolving and spinning. In a typical continuous process, monomer, water and initiator are fed to a continuously stirred overflow reactor. The slurry of polymer, water and unreacted monomer is filtered or centrifuged, the polymer washed and dried, and monomer is recovered from the filtrate and returned to the reactor.

In the UK a high quality fibre is required that is clean and white and this requirement determines the choice of the continuous solution polymerisation process. The polymer is wet spun directly from solution. The fibre produced typically comprises of 90% acrylonitrile, 6-9% methyl acrylate and about 1% acidic monomer.

A high quality fibre requires an acrylonitrile feedstock that is free of the impurity oxazole. It is therefore necessary to purify the acrylonitrile by passing it through an ion exchange resin. This process generates some loss of acrylonitrile when the resin bed is periodically regenerated with dilute sulphuric acid.

Introduction	Techniques fo	r pollution contro		Emissions			Impact		
In-process controls Emissions controls Manager	ent Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

The reaction stage consists of a continuous feed of acrylonitrile, monomers, dyesites, initiators, colour improvers and solvents, such as sodium thiocyanate solution, to the reactor. Unreacted acrylonitrile in the polymer is removed by multi stage evaporation (demonomerisation) prior to the spinning stage, so that acrylonitrile vapour concentration in intermediate storage facilities and at the spinning bath stage is acceptable. The condensed vapours from the initial evaporation stages are recycled to the reactor, whilst those from the latter stages are often waste streams requiring treatment.

The spinning stage extrudes the polymer solution through a spinneret and into a counter-current washing stage in which water washes the solvent from the fibre. The wash liquor is passed to a solvent recovery process.

The fibre is steam stretched, water washed, dyed, a surface lubricant added, dried, an anti-static agent added, crimped and packaged for sale. Vapours are released during these processes by evaporation from the surfaces of the various liquid baths and from the dryer exhaust.

The solvent recovery process concentrates, using a multi-stage evaporator, the weak solvent solution from the washing stage so that the solvent can be recycled. Evaporated water containing traces of organic impurities is condensed and sent for disposal. The concentrated solvent contains impurities that must be removed before recycle and these require a further three recovery stages; sulphate removal, iron removal and the removal of soluble impurities.

Sulphate removal is by the addition of barium carbonate to precipitate barium sulphate which can then be filtered. Iron removal is by an ion exchange resin column. Regeneration of the column generates a waste stream.

Removal of soluble impurities is achieved by the Solvex process. The Solvex process consists of an initial absorption column where the weak solvent (sodium thiocyanate solution) is contacted with di-isopropyl ether and sulphuric acid to extract a top ether phase containing the purified thiocyanate as thiocyanic acid and a bottom waste aqueous phase.

The purified sodium thiocyanate is regenerated from the ether phase by contacting with caustic soda solution. This creates an ether phase that can be recycled and an aqueous solvent phase which, after air stripping to remove the ether, is suitable for recycle to the reaction stage.

Potential emissions to air:

- Monomers from reaction and demonomerisation systems.
- Monomer, fibre and solvent from spinning sections and fibre treatment.
- Monomers from solvent recovery.
- Ether from sodium thiocyanate purification.

Potential emissions to water:

- Streams containing monomers from solvent recovery plants, ion exchange plants, and demonomerisation.
- Streams from solvent purification.
- Effluent from dye baths and rinses.

Potential solid waste streams:

- Spent ion exchange resins.
- · Wastes from solvent recovery plant.

2.1.7.6 Acrylonitrile-butadiene-styrene (abs) copolymers

There is a wide range of these copolymers. The production of nitrile rubber is given as an example of the process type.

Management

Emissions Energy

Installation issues

Closure

Nitrile butadiene rubber (NBR) is produced by co-polymerisation of butadiene and acrylonitrile. Different grades are produced by varying the acrylonitrile: butadiene ratio. Complete conversion of monomer to polymer does not occur and so a monomer recovery and product purification/processing stages are required.

The initial stage of the process involves co-polymerising acrylonitrile and 1,3 butadiene to give a homogeneous co-polymer by free radical polymerisation. Water and an emulsifying agent are added along with modifiers, such as chain transfer agents, and inhibitors to control the extent of polymerisation.

NBR may be produced by either a continuous or batch process.

In the batch process the polymerisation typically occurs in one vessel and then the product is transferred to a second vessel where monomers are recovered by vacuum treatment. Butadiene comes off initially and can be recovered and recycled. Most of the acrylonitrile is then removed but some is left to prevent polymer degradation which would result in the production of a solid waste and fouling of the process vessels.

In the continuous process several continuous stirred tank reactors are used in series with the inhibitor and stabiliser added at the last reactor. A flash vessel is used to remove butadiene. The pressure is then lowered and the product mix steam stripped to remove the acrylonitrile. The overheads are condensed to recover the volatile monomers from the gaseous stream. Water, acrylonitrile and butadiene can be recovered

The product mix in latex form can either be sold or sent forward for further processing as required. Acrylonitrile will be vented from this intermediate storage and requires treatment to minimise emissions.

For further processing the latex is transferred to a coagulation vessel where inorganic salts and small quantities of mineral acids are added as coagulating agents. After a precipitating agent has been added dilute caustic soda is commonly used to remove the emulsifying agent.

The precipitate of nitrile latexes is washed, filtered, washed again and then continuously fed to a dryer. The water washings will contain small quantities of acrylonitrile and fines (non-coagulated polymer) which are removed.

Drying the coagulated solid nitrile rubber will release some acrylonitrile. Drying methods employed include drying drums, band dryers and drying screws. Powder, such as talc or magnesium stearate, can be used to avoid agglomeration of the material and adherence to dryer surfaces. The choice of drying method depends largely on the properties required of the final nitrile rubber.

Potential emissions to air:

- Monomer in vents from reactor, vacuum systems, vent treatment systems.
- Monomer and particulates in vents from powder handling systems and drier.

Potential emissions to water:

- emissions from vent treatment equipment.
- Monomer and polymer in latex wash water.

Potential solid waste streams:

Polymer from vessel cleaning.

2.1.7.7 Polyethylenes

There are several types of polyethylene produced, of which the main groups are:

- Low density polyethylene (LDPE).
- Linear low density polyethylene (LLDPE).

· High density polyethylene (HDPE).

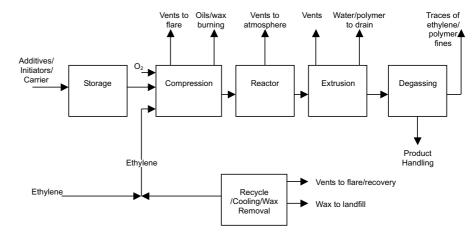
For each type of product there are several licensed processes available. Considerable technical development by producers continues globally, with new catalysts and processes aimed at providing attractive properties to customers and consumers. Awareness of emissions of ethylene has increased in recent years because of its relatively high photochemical ozone creation potential, in spite of being substantially non-toxic. Co-monomers (usually olefins) are used for some products, but this does not substantially affect the environmental impact of the processes.

LDPE Processes

LDPE is produced by polymerising ethylene using free radical initiators such as oxygen or organic peroxides. Operating pressures are high, at 2000-3000 barg, and cooling is used to keep temperatures below 350°C at which ethylene might decompose. Processes fall into two categories: autoclave or continuous tubular reactor. A characteristic feature of older LDPE plants is the decompression, or "decomp". These occur when ethylene decomposes in hot spots and the reactor vents violently. Computerised control minimises the occurrence of this phenomenon.

A typical LDPE block diagram is shown in Figure 2.17.

Figure 2.17: LDPE production



LLDPE/HDPE Processes

Several LLDPE processes are also capable of producing certain grades of HDPE on a swing basis. Low pressure conditions are employed, with Ziegler-Natta catalysts or supported heavy metal oxide catalysts. Metallocenes - a new class of Ziegler-Natta catalysts - have been the focus of much of the recent technical development. Most modern catalyst systems are usually sufficiently active to avoid the need for de-ashing.

There are three basic types of process: gas-phase, solution, and slurry. The solution and slurry processes employ hydrocarbon solvents and tend to have more purge streams than gas-phase plants. These include waxes, solvent purges, and waste-sieve materials.

HDPE process

Processes dedicated to HDPE are usually intended to produce high molecular weight material suitable for blow moulding. Both slurry phase and gas phase processes are available.

Potential emissions to air:

- · Purges of feedstocks or solvents, or the products of their combustion.
- · Hydrocarbons from raw material storage, degassers, extruders, driers and hoppers.
- · Fugitive losses of feedstock and solvent hydrocarbons.
- Vents from catalyst preparation systems, possibly with organometal content

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• Vents at high pressure (LDPE).

Special control techniques include:

- Computerised control on LDPE plants to reduce occurrence of decompressions.
- · Recycle of purge streams for process use or fuel.
- Catalytic oxidation of vents from degassers etc.
- Underwater face cutters
- · Use of high integity equipment and fittings where gases and volatile liquids are handled, plus LDAR.

Potential emissions to water:

Wash water or pellet system overflow.

Potential solid waste streams:

- Off-specification product.
- Waxy or heavy liquid purges.
- Organometallic compounds from catalysts.

Special control techniques include:

- Beneficial use of hydrocarbon residues, including as fuel
- Use of high activity catalysts.

2.1.7.8 Polypropylene

Polypropylene is produced by polymerising propylene. Homopolymer grades are produced from propylene alone, while copolymers incorporate another monomer such as ethylene. Random copolymer and high impact copolymer supply different market needs.

The three main types of polypropylene process are gas-phase, bulk, and slurry. The catalysts have been improved in four generations of development, and de-ashing should not be required on any modern process. A lower grade polypropylene, termed atactic, is typically produced in small quantities from the slurry process, but can usually be sold for adhesive or other uses.

Examples of the three process types are described below.

Bulk liquid process

This uses a continuous single stage polymerisation reaction to produce homopolymers only. Liquid propylene is dried using molecular sieves and treated with copper and zinc oxide catalyst. The catalyst is prepared under high purity nitrogen. Liquid propylene and small amounts of catalyst components and hydrogen are metered into the polymerisation reactor where the solid polypropylene particles are formed as a suspension in liquid propylene. There are no significant by-products from the reaction. The liquid propylene is evaporated from the propylene polymer mixture and the polymer is collected by cyclone and bag filter systems. Polymer powder is nitrogen stripped and then fed to the extrusion unit.

Potential emissions to air:

- Propylene and particulate matter from vents (on dust extraction, extruder, extruder extract).
- Propylene/propane from powder vessel vent, which is generally thermally incinerated.
- VOCs from extruder extract vent.
- · Polymer dust from granulate transport air.
- Bleed streams for which no further recovery or use is practical.

Potential emissions to water:

- Polypropylene from granulate water tank overflow, extrusion floor washings.
- Hydrocarbons from molecular sieve regeneration liquid.

Inorganic salts from vents scrubbing and/or wash waters.

Potential solid waste streams:

- Spent molecular sieves from olefin pre-drying.
- Polypropylene powder from powder vessel cleanout.
- Polypropylene additives from vacuum cleaning of solids.
- · Copper and zinc oxide from spent catalyst packs.

Gas-phase process

Propylene is dried over aluminium oxide and polymerised in a gas phase reactor, using a catalyst and activator. Catalyst is pre-treated with propylene in heptane. Propylene and ethylene are used if a co-polymer is required. Polypropylene powder from the reactor is separated and deactivated using nitrogen, isopropanol and steam. The deactivated powder is transported to granulation under nitrogen, mixed with additives, extruded and chopped into granules under water.

Potential emissions to air:

- Propylene, propane, heptane and pentamethyl heptane from splitter purge vents and intermittent gas vents.
- · Hydrogen chloride from deactivation vent.

Potential emissions to water:

- Sodium hypochlorite, polypropylene from aqueous waste.
- Nalfloc from cooling tower.

Potential solid waste streams:

- Aluminium oxide from spent catalyst.
- Polypropylene from process waste.
- Hydrocarbons from oil/water separator drainings.

Slurry Process

In the slurry process, a hydrocarbon diluent such as n-heptane is used. The reaction conditions are modest, at 60°C, 12 barg. Catalyst and co-catalyst slurries are prepared with solvents and metered continuously to polymerisation reactors.

Potential emissions to air:

- Purges of feedstocks or diluent, or products of their combustion.
- Hydrocarbons from raw material storage, degassers, extruders, driers and product hoppers.
- Fugitive losses of feedstock and diluent hydrocarbons.
- Vents from catalyst preparation.

Potential emissions to water:

Wash water or pellet system overflow.

Potential solid waste streams:

- Atactic polypropylene (if not sold).
- Off-specification polypropylene.
- · Heavy ends from solvent recovery.
- Organometallic compounds.

Special control techniques for poly propylene include:

- Recycle of purge streams to process plant or for fuel use.
- Catalytic oxidation of other significant vents.
- Use of high integrity equipment and fittings where gases and volatile liquids are handled, with LDAR.
- Underwater face cutters.

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- Beneficial use of hydrocarbon liquid or solid residues, including as fuel.
- Use of modern catalysts to avoid de-ashing and to minimise atactic formation.

2.1.7.9 Resins

Resin is a general term used for a wide range of organic polymers including some described above.

Resins are typically manufactured in essentially closed batch reactors operating at temperatures up to 300°C and pressures ranging from vacuum up to 10 barg., although where low boiling monomers such as butadiene, ethylene and vinyl chloride are used the pressure can be up to 100 barg.

The monomers are either charged to a pre-mix vessel or directly to the reactor. If a solvent or water is being used then this is normally charged to the reactor first. Additives such as catalysts/initiators and stabilisers are fed to the reactor and the reaction started. As the reaction proceeds, further additions of all raw materials are made, although if it is a fusion reaction all the monomer is added initially. Some reactor vents are caustic or water scrubbed.

After the reaction has finished, or been stopped, the charge is often fed to an intermediate vessel for dilution, further additions or blending. The product is either filtered to produce the liquid form or dried and/or flaked by such means as a belt flaker to produce the solid form.

Polyester/alkyd products use vegetable oils, fatty acids, polyols and acids as monomer raw materials. The alkyds can be modified with a variety of compounds.

Epoxy ester products use fatty acids and epoxy resins (usually reaction products of epichlorhydrin and diphenylol propane) as monomer raw materials.

Rosin-based resins use rosins, polyols, anhydrides, alkaline earth oxides and phenols as monomer raw materials.

Polyamids use acids and amines as monomer raw materials. Amino resins use acids, alcohols, urea and amines with formaldehyde as monomer raw materials.

Phenolic resins use phenols, cresols, xylenols and formaldehyde as monomer raw materials.

Potential emissions to air:

 Solvent and monomers from storage, reactor systems, intermediate vessels, filtration, solidification equipment, and product packing out.

Potential emissions to water:

- Solvent polymer and monomer from reactor and vessel cleaning, and filtration.
- Spent scrubbing liquor containing solvent and monomer products.

Potential solid waste streams:

- Filtration residue and media.
- · Polymerised solids from reactor fouling.
- Non-recyclable gelled resins.

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2.1.8 Environmental Performance Indicators

Indicative BAT requirements for Environmental Performance Indicators

- 1 The operator should demonstrate that there are in place methods of monitoring and benchmarking environmental performance, with reviews on at least an annual basis. Plans for minimising environmental impacts based on the chosen indicators should be incorporated into on-going Improvement Programmes. The indicators suggested are based on tonnes of organics produced (t_{OP}) and most can be easily derived using the H1 database tool. The limitations of using impact per tonne of organic produced ("impact"/t_{OP}) as a benchmark are understood - clearly they cannot be used to compare companies whose product type differs significantly - but they provide a good basis for measuring performance within an installation or a single company year on year .
 - Specific air quality impact from activities other than from net imported electricity use. (kg/ $\rm EAL/t_{OP})$
 - + Specific air quality impact from net imported electricity use. (kg/EAL/ $t_{\mbox{OP}}$)
 - Specific global warming impact from activities other than from net imported electricity use. (GWP/ $t_{\rm OP})$
 - Specific global warming impact from net imported electricity use. (GWP/ t_{OP})
 - Aquatic impact . (kg/EAL/ t_{OP})
 - Specific potable water use. (t/ t_{OP})
 - Specific non-potable water use. (t/t_{OP})
 - Specific raw material use. (t/ t_{OP})
 - Waste Hazard Score (from H1). (t/ t_{OP})
 - + Waste Disposal Score (from H1). (t/ $t_{\mbox{\scriptsize OP}}$

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2.2 Emissions control

2.2.1 Point source emissions to air

The nature and source of the emissions expected from each activity is given in previous sections and will be confirmed in detail in the Operator's response to the emissions inventory.

The following abatement techniques should be used after measures for prevention and minimisation have been applied. They are described in greater detail in the horizontal BREF on Waste Water and Waste Gas Treatment in the Chemical Sector (see **BREF on Waste Water and Waste Gas Treatment.**).

The selection of BAT for a specific installation will depend on many factors including;

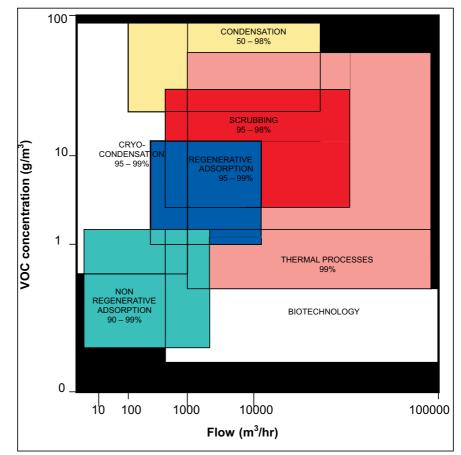
- Gas flow rate (average rate, range, rate of variation)
- Pollutant types and inlet concentrations
- Presence of impurities (e.g. water, dust, corrosives)
- Concentration required in the exhaust
- Safety
- · Investment and operating cost
- Plant layout
- Availability of utilities

Depending on these factors, a combination of techniques may be needed to satisfy the requirements of BAT.

The applicability of these techniques for the control of VOC emissions is summarised in **Figure 2.18** below.

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Figure 2.18: Applicability of abatement techniques to VOC flow rate and concentration [Environment Agency (E&W), 1999 #6]



2.2.1.1 Condensation

Potentially, condensation is the simplest technique for recycling substances in the gas phase and minimising waste. Where appropriate condensation should receive strong consideration as the primary abatement technique, for example upstream of plant scrubbers.

Condensation is generally achieved by indirect heat exchange, e.g. in a shell-and-tube heat exchanger, with cooling water, possibly chilled. Coolant temperature should be justified with reference to the vapour quantity discharged. Some systems operate down to -75°C using a series of refrigerated condensers with progressively lower temperatures to prevent process blockage. The use of scraped heat exchangers should also be considered. Where liquid nitrogen is used as a source of blanket gas, its evaporation can provide integrated refrigeration to cryogenic temperatures.

Monitoring of cooling fluid temperature and flow are required to assess the efficiency of the condenser. A low- flow alarm and coolant high-temperature or exit vapour stream high-temperature alarm, or equivalent, should be required to register upset conditions likely to affect the performance of the condenser.

For the specific case of a reflux condenser on a batch reactor, the cooling capacity of the condenser should, where possible, be in excess of the heating capacity of the reactor, as well as being capable of achieving the desired vent temperature.

2.2.1.2 Absorption

This is a common method for the removal of soluble components of a gas stream. The absorbent or scrubber liquor can be water, caustic, acidic or other neutralising substance or oxidising reagent according to the nature of the contaminants to be removed. The absorbent may be recycled round the absorber or passed to a recovery system.

To achieve optimum transfer from the gas phase to the liquid phase it is important that:

- · Maximum interfacial contact between gas and liquid phases is maintained
- · Sufficient residence or contact time for absorption is allowed; and
- · The contaminant is readily soluble in the absorbent

In most cases the absorbent flows counter-currently to the exhaust gas so that the most dilute gas is contacted with the most pure absorbing liquor, providing a maximised concentration difference for the entire length of the column. This arrangement results in the highest theoretical removal efficiency.

A standard process for recovering solvents from waste air streams uses a combination of: absorption to absorb the vapours into a liquid stream; distillation or degassing to separate the resulting mixture into its individual components; and condensation to recover the solvents in a usable form. It should be noted that wet collection devices can be used for these purposes as well as for particulate matter control.

Consideration should be given to using an absorbent that can be used directly in the same process, for example by using an appropriate raw material or solvent as the absorbent to recover solvent or partially reacted products such that they can be recycled to the process, or used elsewhere. Absorption of solvents into oil is a very effective recovery method for those solvents possessing lipophilic properties, especially halogenated organic solvents such as dichloromethane.

Instrumentation and alarms should be installed to ensure that liquid level and flowrate are maintained and that the pressure drop remains constant. Low-temperature alarms may be necessary to warn of freezing. Concentration of absorbent should also be monitored. Scrubbers should include sample points upstream and downstream to allow analysis of inflow and outflow gas concentrations.

Packed and Plate Tower Scrubbers

In a packed tower scrubber the packing material provides a large surface area for mass transfer between liquid and gas phases. In the plate column the plate disperses the gas into numerous bubbles, so creating a large surface area for mass transfer.

The even distribution of scrubbing liquor and prevention of plugging or channel flow is of critical importance to the satisfactory operation of such a system.

The advantages of packed tower scrubbers include generally modest to low pressure drops, and ease of construction with chemically resistant material.

Packed tower scrubbers are generally best suited to situations where a high gas removal efficiency is required and the exhaust gas to be treated is relatively particulate-free. Plate column scrubbers are more effective for dealing with gas streams containing particulate material and can more readily accommodate fluctuations in flowrate and temperature. Fluidised-bed packed towers are particularly effective at overcoming solids blockage problems.

Where a scrubber is used for odour control the absorbent is often an oxidising reagent such as potassium permanganate or sodium hypochlorite.

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Spray Towers

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materials

Spray towers can achieve good removal rates for readily absorbable contaminants. Mass transfer is achieved by atomising the absorbent using nozzles and may be enhanced by the use of appropriate surfactants. The simple design allows relatively easy construction in corrosion-resistant material and ease of maintenance.

Accidents

The advantages of these units include cheapness and minimal energy requirements due to low pressure drop. However, regular checks should be made to ensure that the nozzles are neither excessively worn nor clogged, particularly if the gaseous stream contains particulates. Where appropriate, pressure gauges should be installed.

Specialist spray scrubber designs, using high-pressure liquor, can treat gases to plate tower standards without fouling or solid blockage problems.

Wet Mop Scrubbers and Rotaciones

In wet mop scrubbers, absorbent is injected into the impeller casing where it is atomised and mixed with an extracted air stream. The impeller is usually of an absorbent and flexible fibrous material. The exhaust stream is demisted and the absorbent either discharged to drain or recirculated to the impeller casing via a holding tank.

Rotaclones operate in a similar manner to wet mop scrubbers except that the impeller is rigid. Rotaclones tend to be used for higher flowrates, wet mop scrubbers for lower ones.

2.2.1.3 Adsorption

Adsorption describes the removal of gaseous components from a gas stream by adherence to the surface of a solid. The gas molecules removed are referred to as the adsorbate and the solid to which the molecules adhere is the adsorbent. The most common adsorbents are activated carbon, silica gel, activated alumina and zeolites.

The polarity of the surface of the adsorbent determines the type of vapours for which the adsorbent has the greatest affinity. Polar adsorbents will preferentially adsorb any water vapour present in the gas stream. Since moisture is present in most gaseous waste streams from the organic chemical industry, their application to pollutant removal is limited. Activated carbon is the only common non-polar adsorbent. It is used to control emissions of organic solvents, odours, toxic gases, acid vapours, phenols and hydrocarbon vapours.

Adsorption is an exothermic process; therefore, carbon adsorption may not be an appropriate technique for highly concentrated streams of organic compounds with high heats of adsorption e.g. ketones. The molecular weights of the compounds to be adsorbed are generally in the range of 45-130. Properly operated adsorption systems can be very effective for homogeneous off-gas streams, but may be unsuitable for a multicomponent system containing a mixture of light and heavy organics. The presence of water can severely reduce reclamation efficiency. The lighter organics tend to be displaced by the heavier (higher-boiling) components, reducing system efficiency.

Activated carbon absorption

Activated carbon beds can generally be used within the processes covered by this Note to control emissions from storage tanks and can often be used as a polishing treatment after condensers and scrubbers.

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Carbon adsorption systems usually take the form of multiple-bed systems, with one on-line, one regenerating and one on stand-by. The contaminated gas stream should be pre-treated to remove any particulate matter or entrained liquids. The gas stream is then passed down through the fixed carbon bed. Upward flow through the bed is usually avoided because of the risk of entraining carbon particles in the exhaust gas.

As the temperature increases, the capacity of an adsorbent decreases and adsorbers generally operate below 55°C. Any increase in pressure will increase the adsorption capacity of a system. The residence time in the adsorber is dependent on the gas velocity and the size of the adsorber unit. Consequently, providing sufficient bed depth and low gas velocity are important design factors.

High humidity can interfere with the adsorption process. Similarly, other entrained compounds and particulate matter interfere with the adsorption of gas molecules. The humidity levels, temperature and pressure during the adsorption should be monitored to maintain optimum efficiency.

It is essential to measure the performance of adsorption equipment, i.e. sample points should be in place to facilitate the analysis of inflow and outflow gas streams. The adsorption equipment should be monitored for breakthrough. Similarly, other parameters such as temperature and pressure should be monitored.

Regeneration of carbon beds

Periodic regeneration of the adsorbent bed is required to maintain removal efficiencies. This may be achieved thermally by steam stripping and condensation followed by recovery of the organic material by phase separation or distillation. The water stream may be contaminated and need treatment. An option for regenerating carbon beds that eliminates waste water associated with steam is to pass hot combustion air for an incinerator through the carbon bed. The desorbed organics are carried in a concentrated stream to the incinerator and burned as fuel, decreasing or eliminating the need for auxiliary fuel. However, it should be remembered that re-use of the adsorbate is the preferred option.

Pressure reduction may also be used to desorb the organic material from the bed. In a few cases it may be appropriate to displace the adsorbate with a more strongly adsorbed material.

Eventually, carbon loses its ability to be regenerated in situ, because of residual organic compounds. It should then be returned to the supplier or a third party for regeneration in preference to disposal as waste.

2.2.1.4 Biofiltration and Bioscrubbing

Biofiltration generally uses beds of organic materials such as peat, heather, bark or some composts. Bioscrubbing on the other hand takes place in towers containing a bioflora.

In biofiltration, waste gases pass through a filter reactor in which micro-organisms are fixed in a water phase within the filter material. The water content within the filter is critical to its effectiveness and, since the gas flow through the reactor will tend to evaporate it, a humidification stage is often included upstream of the biofilter.

Hot gases may need to be cooled closer to the optimal activity temperature for aerobic microorganisms, generally 25 to 35°C. The potential temperature rise across the bed of up to 20°C should be taken into account.

Biofiltration and bioscrubbing have lower operating costs than many other air pollution control technologies for treating low concentrations of biodegradable organic pollutants. They are used in particular for the abatement of odorous emissions. Bioscrubbers have the higher maintenance cost of the two. Environmental benefits include low energy requirements and the avoidance of cross-media transfer of pollutants.

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The major operating parameters such as the off-gas temperature and back-pressure should be checked daily. Similarly the moisture content in the filters should be monitored regularly. A low-temperature alarm should be fitted to warn of freezing, which may damage the filter and may affect the growth of the microbial population.

Consideration should be given to the effect of loss of biomass due to the introduction of toxic compounds and a stand-by procedure should be developed for such an event.

2.2.1.5 Decomposition

Thermal or catalytic decomposition processes should be considered for non-biodegradable, toxic pollutants in the gas phase where further recovery cannot be achieved.

Four basic decomposition processes can be employed: thermal incinerators, catalytic incinerators, flares and process boilers. The applicant should justify the choice of process.

On all types of thermal decomposition equipment, sampling points should be in place for monitoring the performance of the combustion process. Several parameters should be continuously monitored. These should include flame failure, which should trigger an alarm, the combustion temperature and pressure.

Thermal Incineration

Thermal incinerators are used to control waste gases containing low concentration of organic vapour.

The temperature of the incinerator and the gas residence time are the most important operational variables. The calorific value of constituents in waste streams also varies and a supplementary fuel may be required. Heat recovery is important in minimising fuel use and cost. Recuperative or regenerative systems are widely used. Reference should be made to the Waste Incineration Guidance Note for achievable release levels.

Catalytic Oxidisers

The inclusion of a catalyst in an incineration process allows the oxidation reaction to take place at a lower temperature and at a faster rate than in a thermal incinerator. However, catalytic oxidisers tend to be less robust: waste streams containing particulate matter cannot be destroyed effectively in a catalytic incinerator since particles may blind the surface of the catalyst. Similarly, catalytic oxidisers can be affected by waste gas constituents, e.g. acetic and acrylic acids or poisoned by sulphur compounds.

All catalysts deteriorate with use and need to be replaced periodically. The performance of the catalyst should be monitored regularly so that any deterioration is noted at an early stage and remedial action taken. A safe disposal route for the catalysts should be identified. In many cases the catalysts are returned to the manufacturer for regeneration.

Flameless Thermal Oxidisers

These allow oxidation at reduced temperature by passing the waste gas through a preheated ceramic packing. In the absence of a flame, formation of NO_X is reduced. A similar effect may be achieved in a regenerative system operating under autothermal conditions.

Flares

Direct combustion or flaring can be used for the destruction of intermittent or emergency emissions of combustible gases. Whilst there is no suitable alternative to a flare system for dealing with emergency reliefs, deliberate continuous flaring of process vents should be discouraged as there is insufficient control over the combustion exhaust gases.

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The flare system should be carefully designed to allow combustion of all gases necessarily vented to it under all circumstances. The basis of the worst case should be justified. The effect of low gas flow and wind dilution should be considered and allowed for in the design. Flares should burn without smoke under all conditions and should be designed to accommodate varying flowrates. The applicant should justify flare heights. Knock-out pots/drums should be installed as close as practicable to the flare to catch liquids and condensible material.

Problems associated with flare systems include:

- The heat generated may be unacceptable without careful design
- The light/luminescence of the flame may be a nuisance if the plant is near an urban settlement, and concealed combustion chambers/ground flares should be considered in such cases
- Flare tip mixing systems can cause increased noise levels
- Incomplete combustion of organic compounds
- Both oxygen starvation and oxygenated flames can give rise to emissions of toxic or obnoxious substances
- · The flaring of halogenated substances should be avoided
- Flares need to be kept lit constantly with robust pilot light and flame failure alarms should be installed on pilot lights
- · Heat cannot be recovered
- · Constant purging is generally required, and
- Monitoring of emissions from flares is generally impracticable, making it difficult to ensure adequate combustion.

Flare gas recovery systems should be considered to minimise flaring.

2.2.1.6 Particulate matter abatement techniques

The methods available for minimising or reducing discharges of particulate matter to the atmosphere are briefly described below. The appropriate technique depends on the characteristics of the particles and the carrier gas stream, process factors such as temperature and pressure, and operational factors including structural limitations such as floor space and head room.

Further information is available in the Waste Water and Waste Gas treatment BREF.

Cyclones

Cyclones are the principal type of gas-solids separator employing centrifugal force, and are widely used. They can be manufactured from a wide range of materials; and can be designed for high-temperature and pressure operation. Cyclones are suitable for separating particles down to about 5 um; smaller particles down to about 0.5 um can be separated where agglomeration occurs. High-efficiency cyclones are capable of removal efficiencies of the order of 90% for particles down to 5 um. At smaller particle sizes the collection efficiency drops off appreciably. High-gas-rate cyclones have a removal efficiency of about 90% for particle sizes down to about 20 um. The most commonly used design is the reverse flow cyclone, where gas enters the top chamber tangentially and spirals down to the apex of the conical section. It then moves upward in a second, smaller-diameter, spiral and exits at the top through a central vertical pipe. Gas pressure drops tend to be of the order of 10-70 mm water gauge.

Fabric Filters

The industrial fabric filter is generally constructed from a woven material or a felted fabric to provide the filtration medium through which the particle-laden gases are passed. Fabric filters are particularly useful as secondary or tertiary gas cleaning devices with a cyclone, dry scrubber or fluidised-bed absorber located upstream.

Filter efficiency may be enhanced by pre-coating the filter cloth prior to being brought on-line.

Fabric filters are not generally suitable for use in moisture-laden streams or those with acidic, tarry or sticky characteristics due to the adverse effects of fabric "blinding" and adherence problems. Regular maintenance and cleaning of the filters is necessary to maintain removal efficiencies.

The performance of the fabric filters may be monitored by measuring the dust concentrations upstream of the filters and in the exhausted gas stream. Bag failure should be alarmed using, say, an opacity meter, or particle impingement detector or by appropriate pressure drop monitoring.

Ceramic Filters

Ceramic filters are constructed in two varieties: high-density and low-density. The high-density unit comprises a silicon carbide base with a fine coating (usually aluminium silicate). The low-density unit comprises a matted mixture of silica and alumina fibres.

The high-density units generate a higher pressure drop than the lower density type. They are both capable of withstanding temperatures up to 900°C and instantaneous temperature shock from 900°C to 0°C. Filtration efficiencies greater than 99.9% for particulates down to sub-micrometre sizes are attainable. Regeneration is achieved by reverse air pulse at about 7 barg, an operation similar to that undertaken with bag filters.

Wet collection devices

Wet collection devices use a variety of methods to wet the particles to remove them from a gas stream. The technology available varies in terms of cost, collection efficiency and energy requirements. Increased energy results in increased collection efficiency for particulate matter. They include venturi, jet, dynamic, centrifugal and impingement scrubbers but generally only the first two are suitable for submicrometre particles.

Wet collectors have a constant pressure drop and do not present secondary dust problems. However the design should ensure that mists and fumes cannot be formed. They can handle high-temperature gas streams, moisture-laden gas streams, corrosive gases and aerosols.

In a venturi scrubber the gases are drawn into the throat of a venturi tube to which pressurised water is injected. There are two basic types: low and high-pressure drop. Pressure drops at the lower end of the range (250 mm water gauge) are generally adequate for the removal of particles of a few micrometres in diameter. For sub-micrometre particles the upper range of the pressure drops (1500 mm water gauge) may be required particularly if better than 99% collection efficiencies are required.

The performance of scrubbers should be measured by analysis of the exhausted gas and of the scrubber liquor. The pressure drop across the scrubber and the level of scrubber liquor should also be monitored.

Dust Suppression Equipment

Wherever possible raw materials should be contained in silos, storage tanks, or covered areas. The storage of dusty materials by stockpiling requires some form of dust suppression. Continual maintenance of a sufficient moisture level on the surface of stockpiled dusty material may be necessary to arrest dust pollution.

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Indicative BAT requirements for the control of point-source emissions to air

- 1 The benchmark values for point source emissions to air listed in **Section 3.2.1** should be achieved unless alternative values are justified and agreed with the Regulator.
- 2 The main chemical constituents of the emissions should be identified, including VOC speciation where practicable.
- 3 Vent and chimney heights should be assessed for dispersion capability and an assessment made of the fate of the substances emitted to the environment (see Section 4).

Control of visible particulate plumes

4 Even where particulate benchmarks are already met, the aim should be to avoid visible emissions. However, because plume visibility is extremely dependent on the particle size and reflectivity, the angle of the light, and the sky background, it is accepted that, even when BAT is employed and very low emissions are being achieved, some plumes may still be visible under particular conditions.

Control of visible condensed water plumes

- 5 The need to minimise water vapour plumes should always be considered as, in addition to possible local visual amenity issues, in severe cases, plumes can cause loss of light, fogging, icing of roads, etc. High moisture content can also adversely affect plume dispersion so, where practicable, water content of the exhaust stream should be reduced. Ideally, the exhaust should be discharged at conditions of temperature and moisture content that avoid saturation under a wide range of meteorological conditions, including cold damp conditions.
- 6 The use of **primary energy** to reduce a plume simply because it is visible is not considered BAT. However, it may be appropriate to use **waste or recovered heat**, for example, heat in a gas stream prior to wet scrubbing can be used for re-heating the exhaust stream after scrubbing by means of a gas-gas heat exchanger. The use of energy for exhaust gas re-heat should be balanced against the benefits gained.

2.2.2 Point source emissions to surface water and sewer

The nature and source of the emissions to surface water or sewer expected from each activity is given in previous sections and the inventory of emissions should be confirmed in detail in the Application.

As noted before, the primary consideration should always be to prevent releases of harmful substances to the aquatic environment, whether releases are direct or via a sewage treatment works, and only where prevention is not practicable should the release be minimised or reduced to the point where the emission is incapable of causing significant harm.

2.2.2.1 General

Waste water can arise from the process, from storm water, from cooling water and from fire-fighting. It may be contaminated by accidental emissions of raw materials, intermediates, products or waste materials. It is very common for the aqueous effluents from several process plants to be treated

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together, in a site waste-water treatment system or as a combined stream to external treatment. It must be recognised that synergistic effects may occur when effluents are mixed. Acids and alkalis may neutralise each other, for example. A dilution effect may be acceptable if it permits a pollutant to be destroyed in a biological system. However, the dilution effect alone should not be used to achieve permissible final effluent quality. Treatment at the process plant may be required.

The following techniques should be considered for reducing waste-water discharges:

- Minimise the presence of water in the process including water used in or produced as a by-product
 of reactions, product purification and equipment cleaning
- Recycle waste-water back to the process or to secondary uses such as equipment wash-down, using water pinch analysis if applicable
- Employ indirect contact heat exchange devices
- Segregate process water, storm water, and indirect cooling water streams to reduce the hydraulic loading to waste-water treatment equipment or sewers
- Develop spill contingency procedures to minimise the risk of accidental release of raw materials, products and waste materials and to prevent their entry into water
- Use dry cleaning methods wherever practicable for solids. Vacuum extraction reduces the loss of
 product to the waste-water and, in some cases, allows the recovery of these products
- · Wipe down equipment that is accessible, rather than washing and rinsing it

The characteristics of emissions to water from a plant largely depend upon the type of process involved, the standards of housekeeping, the degree of recycling achieved and whether or not potential emissions to air are transferred into the aqueous media, e.g. by gas scrubbing. Aqueous wastes may contain a wide range of organic compounds as well as particulate matter

The neutralisation of an acid waste with an alkaline waste should be considered if compatible streams are available. However, care should be taken to avoid discharging alkaline solutions, contaminated with sulphur compounds, into low- pH waters, because there is a risk of subsequent release of those compounds in gaseous form.

Where appropriate, liquid effluents of different characteristics should be segregated for treatment by the most appropriate methods.

Treatment chemicals such as corrosion inhibitors, descaling agents, sodium hydroxide and biocides should be chosen such that they minimise the release of polluting substances, e.g. use of mercury-free sodium hydroxide

Separated organic chemicals should be skimmed off in a manner that prevents air pollution and, where practicable, should be recycled to the process.

A site-specific spillage contingency plan should be prepared and suitable materials and equipment held on site.

2.2.2.2 Water Collection

Process Waters

Process waters are those obtained as a result of the processes carried on in the installation and arise from specific plant items. Examples include: tank bottom drainings; distillation condensates; purge streams; blow-down waters; and drainage from process, handling and storage areas.

As a consequence of their direct contact with other process fluids, process waters may have absorbed organic compounds and may be emulsified. Accordingly, they should be conveyed from source via an appropriate sewer to treatment plants in a closed system as far as practicable.

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The quantity and nature of contamination will be largely site- specific but can generally be categorised as:

- · Waste-water streams contaminated with hydrocarbons
- · Waste-water streams contaminated with chlorinated hydrocarbons, and
- · Acidic and alkaline waste-water streams

Waste waters containing chlorinated hydrocarbons should where possible be treated separately to ensure proper control and treatment of the chlorinated compounds. Released volatile chlorinated hydrocarbons should be contained and vented to suitably designed incineration equipment.

Potential emissions from vacuum systems should be minimised by the following methods:

- · Vacuum lines should pass through knock-out pots and separators for recycle wherever possible
- The use of process fluids for liquid ring pump sealing should be considered together with the subsequent use of these contaminated streams within the process. Consideration should be given to the use of dry vacuum pumps, which do not use either a sealing fluid or lubricating oil
- Where sealing fluids are used, the installation of closed systems should be considered together with heat-exchange equipment and scrubbing facilities where required

Site Drainage Waters

These are essentially rain water running off hard surfaced process areas or collected by purposedesigned drains. They may be contaminated with organics but are not generally emulsified. Accordingly, they should be passed to a treatment plant, via an oil separator. The site drainage should be designed such that spillages of chemicals, lubricants, etc., should be routed to the effluent system, with provision to contain surges and storm-water flows.

The collection system should also take account of the additional fire water flows (BS 5908 gives guidance), or fire-fighting foams. Emergency storage lagoons may be needed to prevent contaminated fire water reaching controlled waters.

Cooling Waters

Discharges from once-through cooling water systems or other sources should not be used to achieve, by dilution, release limits for pollutants being discharged from treatment plants. Cooling waters are generally used in indirect, recirculatory systems from which a purge stream is taken to control levels of solids etc. In addition to solids, this stream will contain treatment chemicals and any process materials leaked from heat exchange equipment.

2.2.2.3 Treatment Methods

Further information is available in the BREF on Common Waste Water and Waste Gas Treatment. (Reference 1)

It is unlikely that any single waste water treatment technique will be adequate to render harmless the waste water to be discharged. For example, a waste water stream with a low pH and a high organics content would require both pH adjustment and a means removing the organic compounds. Treatment methods including combinations of those below should be applied as appropriate.

In-plant Treatment

- · For heavy metals, combinations of: oxidation/reduction; precipitation; filtration.
- For organics, combinations of; air or steam stripping; granular activated carbon; ion exchange; reverse osmosis; electrodialysis; oxidation, including wet oxidation.

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Primary Treatment

Primary treatment prepares the waste waters for biological treatment. Large solids are removed by screening, and grit is allowed to settle out.

- Neutralisation
- Coagulation/flocculation
- Flotation/sedimentation

Biological Roughing

- Trickling filter
- Anaerobic treatment

Secondary Treatment

This is the biological degradation of soluble organic compounds typically from 50-1000omg/l Biological oxygen demand (BOD)5 to under 20mg/l.

- Aerated lagoon
- Rotating biological contactors
- Activated sludge

Tertiary Treatment

- Filtration
- Ozonation
- Granular activated carbon (GAC) adsorption
- Powdered activated carbon
- Nitrification/denitrification

Sludge Dewatering

Waste solids in slurry form are produced by primary sedimentation, secondary clarification, and various in-plant treatments and pre-treatments. These sludges typically have to be thickened and dewatered before they can be incinerated, landfilled or otherwise disposed of. Methods available include combinations of:

- · Gravity thickening
- Dissolved-air flotation
- Filtration
- Drying
- Centrifugation
- Sludge digestion

Sludge Disposal

Depending on the nature of the remaining sludge this can be disposed of to:

- Incinerator
- Encapsulation
- Land
- Lagoon

In-plant treatments

The following sections describe techniques available for treating the various contaminants.

Immiscible Organic Chemicals/Water Separation

Techniques for separating immiscible organic chemicals and water streams, which could then be treated separately, include:

American Petroleum Institute (API) separators

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- Tilted plate separators
- Electrostatic coalescers
- Dissolved and induced air flotation
- Hydrocyclones
- Use of acceptable physical coalescing agents
- Ultrafiltration; and
- · Surface-modified cellulose filters

Stripping Sulphur Contaminants

Removal of sulphur contaminants can be achieved by steam or air stripping. If the concentrations are low an acclimatised biological treatment system may be more appropriate.

The stripping process is especially useful for process water contaminated with hydrogen sulphide, carbon disulphide, carbonyl sulphide or low-molecular-weight mercaptans.

Contaminated effluent is pumped to the top of the stripper, which can be either a packed tower or a plate column. Steam is injected into the bottom of the tower or, alternatively, the tower may be fitted with a steam-heated reboiler. Overheads are condensed and the condensate is returned as reflux to the column. The sulphide- or mercaptan-rich gas passes to a sulphur recovery unit or to incineration.

The potential emissions can be minimised by the following methods:

- Vents from the feed vessels should be directed to the contaminated vapour treatment system.
- The steam stripper is of critical importance in maintaining final effluent quality and preventing odour problems. Therefore, standby stripping facilities should be provided or valid alternative methods of treatment should be available.

Care should be taken when selecting construction materials, particularly for the column overhead equipment, since severe corrosion can be encountered. Contaminated effluent steam strippers are prone to plugging and sequestering agents are frequently used to prevent calcium deposition. The potential emissions into water arise from inadequate stripping performance.

Sludges will be generated by separation of fines from effluent streams. These may be incinerated or if appropriate, sent to landfill. Solid wastes containing potentially acidic materials should be neutralised prior to disposal to landfill. Such wastes can be mixed with dry lime to neutralise them and possibly reduce their solubility.

The remaining vapour stream may well require further treatment or recovery.

Volatile Organic Compounds

Steam or air stripping can also be used to remove volatile organic compounds from the effluent stream. This will reduce subsequent desorption to atmosphere as well as decreasing the concentration in the effluent. The stripped VOCs require appropriate recovery or destruction. One option is to return air laden with VOC to a boiler or fired heater, provided that combustion conditions are appropriate. For chlorinated organic compounds, recovery is preferred or, if essential, combustion at hazardous waste incinerator conditions.

Neutralisation

Acidic or alkaline effluents should be dosed with an appropriate neutralising agent to achieve the required pH for the receiving water. pH control should be carried out in a vessel constructed of suitably resistant material. The vessel should be designed to allow a suitable retention time for dosing and mixing. Where large discharges of effluent with high or low pH are possible, consideration should be given to a two- or three- stage feed-forward pH control system.

Care should be exercised with acid dosing effluent containing soluble toxic gases. The vent from these vessels should pass to scrubbing facilities.

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Dosing systems are unable to cope with effluents of extreme pH; therefore, an intermediate facility capable of storing strongly acidic or alkaline effluents should be installed with automatic control if such effluents are likely. The control of pH is difficult since the relationship between pH and concentration of reagent is highly non-linear. A better response profile and hence a control of pH is claimed for some reagents. Examples include the use of carbon dioxide, or magnesium hydroxide which are self-buffering. A typical titration curve favours multi-stage dosing. Automatic pH meters should be backed up by regular manual pH measurements and should be calibrated frequently.

Use of other wastes, rather than prime raw materials, should be considered as the neutralising agent.

Solids Removal

The removal of particulate matter from effluent can be hindered by fluctuations in flow. A flow balancing facility may be required upstream of any equipment for the removal of particulate matter. The removal of finely divided suspended solids can be enhanced by the addition of chemical coagulants/flocculants. Similarly, these substances can aid the removal of emulsified organic material. The addition and mixing of pH control chemicals and flocculants can be made, as necessary, prior to raw effluent entering the solids removal tank.

Settlement

Separation of up to 90% of the suspended solids can be achieved by settlement. Settlement is carried out in a clarifier. The clarifier design that is considered to be the most efficient and economical is a circular, mechanically scraped tank. However, depending on the flowrate, one or more pyramidal-type settlement tanks may be appropriate. Control for settlement processes should include a sludge blanket level indicator and high-level alarm. Where scrapers are used, loss-of-motion sensors should be used.

Sludge consisting of readily biodegradable organics containing sulphur will have a tendency to produce hydrogen sulphide unless properly aerated.

Flotation

An alternative to sedimentation is using either induced or dissolved-air flotation, although it is less common in the chemical industry. The required tank size is reduced but more ancillary equipment is needed, making the overall capital cost higher. Controlled release of pressure produces a rising blanket of micro-bubbles as the dissolved air passes out of solution. The bubbles carry suspended solids to the surface of the tank where they are removed by surface skimmers. Retention times are typically of the order of 20-40 minutes at peak hydraulic loading (influent and recycle). Addition and mixing of pH control chemicals and flocculants can be made as necessary prior to raw effluent entering the tank.

Where volatile organic chemicals may be present, the impact of the release to air of any of those chemicals due to the action of aeration needs to be considered.

Adequate control should be provided to monitor the air supply. The skimmers on the surface can be monitored by loss-of-motion sensors.

Precipitation

Precipitation should be considered as a technique for removal of certain compounds, such as those containing heavy metals, which could be recycled or which it is more appropriate to dispose of to land than water.

Control of pH, solid particle growth conditions and residence time are some of the key parameters to be considered. (Where multi-stage precipitation is used, solids separation normally occurs between stages.)

An example of a precipitation system is the removal of mercury from waste waters with one or more hydroxide precipitation stages (at increasing pH) followed by a sulphide precipitation stage with long residence time.

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Dewatering

Raw

Dewatering of sludge wastes is a common method of waste volume reduction.

Mechanical dewatering as opposed to gravity thickening is appropriate for many liquid wastes associated with the manufacture and use of organic chemicals.

A variety of dewatering facilities can be employed including: centrifuges, filter-belt presses, filter-plate presses and rotary vacuum filters. The system choice is dependent on cost, space availability and the degree of dewatering required. An additional dose of polyelectrolyte (1-5 kg/tonne dry solid) may be necessary as a dewatering aid. Such dosing should be optimised.

Dewatering facilities should be situated in enclosed buildings and any noxious fumes emitted should be exhausted via a gas cleaning facility. The filtrate may require treatment prior to disposal.

Filtration

Intermediate or product materials are often isolated as solids. The maximum retention of solids on the filter is required, which, for batch processes, usually involves recycling the initial filtrate until the initial bleeding of solids has ceased. Loss of solids to water should be quantified.

The method of discharging of the solid filter cake varies between each type of filter but it should be demonstrated that the method selected minimises any spillage or loss of solids to the water environment. Means to collect and recycle any spillage should exist that preclude it being flushed to drain.

If the filter requires clean-down, the quantities of solid product lost to the water environment should be defined and shown to be the minimum achievable.

Since the mechanical integrity of the filter medium is crucial to the operation, a means of preventing its failure and consequent loss to the environment is required. This can take the form of a guard filter, collection vessel or an automatic detection and shut-down system.

Where solid impurities are removed from process liquors and become waste, the means for discharging, as well as techniques to minimise their organic contents, and the disposal method should all be justified.

The replacement of filter cloth can generate a significant clean-down stream. Sometimes replacement can be minimised on multi-product plant by storage of used cloths for re-use on each specific product.

For both liquid/liquid separators and liquid/solid separators the retained batch is usually washed, often with a discrete number of washes. Sometimes the last wash of one batch can be used as the first wash of the next batch to minimise the overall usage. The application should show that this technique is used or that it is inappropriate.

Biological Treatment

The treatment of biodegradable material by microbial activity requires detailed consideration of the nature of the waste in order to design an appropriate biological treatment system.

Potential problems of process inhibition due to the presence of toxins can be identified by treatability tests.

A biological effluent treatment plant will be acclimatised to the effluent feed and nutrient conditions. Therefore, under normal circumstances, a flow balancing system or buffer tank is required to balance flows and pollution loads to the plant and to allow analysis to check compatibility prior to treatment.

Biological systems may be aerobic or anaerobic. Typical types include: trickle filter beds (biological filtration); rotating biological contactors; fluidised-bed systems; activated sludge; deep shaft and polishing filters.

For aerobic systems, the use of pure oxygen allows better control with varying loads.

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For biological treatment the pH of the feed should be kept between 6.5 and 8.5 to ensure optimum biological activity.

Consideration should be given to the effect of loss of biomass due to the introduction of toxic compounds, and a stand-by procedure should be developed for such an event. Such a procedure may include maintaining a stock of seed inoculum.

Closed biological systems can reduce volumes of off-gas and odour nuisance.

Activated Carbon Adsorption

Activated carbon columns are employed for the treatment of toxic or non-disposable waste waters and for tertiary treatment following biological oxidation.

Most heavy metals can be removed by use of carbon columns. In order to avoid reduced capacity after regeneration, the carbon should be acid-washed prior to re-use.

Total organic carbon (TOC) can often be reduced by up to 99%.

Powdered activated carbon (PAC) can be added to activated sludge processes to enhance performance. Typical dosage levels are of the order of 20-200mg/l of effluent feedstock. Its usage results in decreased variability of effluent quality; the removal by adsorption of non-biodegradable organics; and the further degradation of normally non-degradable substances.

When there is a small or intermittent application of PAC, the carbon is disposed of with the excess sludge. Continuous application at larger plants, however, requires regeneration of the carbon.

Generally granular activated carbon (GAC) is easier to regenerate, but usage of powdered activated carbon (PAC) offers several advantages. These can include: a more consistent effluent quality; usage and recycling can be integrated into the biological treatment facility at minimal capital cost; and usage can also help to reduce, or eliminate in some cases, the problem of nitrification caused by the presence of toxic organics.

Ion Exchange Resins

Ion exchange can be employed for the removal of undesirable anions and cations from a waste water. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions. Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Ion exchange resins are called cationic if they exchange positive ions and anionic if they exchange negative ions.

Treatment of a waste water by ion exchange involves a sequence of operating steps. The waste water is passed through the resin until breakthrough occurs. The bed is then regenerated by backwashing with water and then regenerant prior to re-use. The disposal of regenerant liquors is an important factor in minimising environmental harm.

Macro-reticular resins are employed for the removal of specific non-polar organic compounds. They are capable of removing between 85 and 99% of Schedule 5(1) substances from waste streams.

Fouling of resins, especially by unexpected organic compounds, needs to be considered.

Electrolytic Exchange

Metals can be extracted from aqueous streams by sacrificial exchange. For example, adding zinc to an aqueous solution of lead salts results in the precipitation of lead, zinc being more electropositive than lead.

This process results in the release of zinc into the aqueous stream. Careful consideration should therefore be given to the concept of BPEO when considering electrochemical exchange techniques.

Membrane Processes

Membrane processes include: ultrafiltration, reverse osmosis, membrane filtration, and pervaporation. The efficiency of the filtration processes depends upon the difference in size between the pore and the particle to be removed or retained; whilst in reverse osmosis the efficiency depends on how well the membrane rejects the flow of solute whilst allowing the flow of solvent.

These types of process can be used either to clean up the waste water for re-use, or to recover material for recycling. They tend to be used in specialist applications where the membrane technology has been developed to overcome membrane life and fouling problems.

Pervaporation is a process that uses polymeric membranes for the removal of organic compounds from water. It is suitable for the treatment of waste water containing VOCs and chlorinated solvents. The component to be separated is "evaporated" from a liquid waste, through a membrane, under vacuum. The separated component is recovered by condensation. A wide variety of organic polymers can be used to remove specific target contaminants. Pervaporation is a technically feasible and economically attractive method for treating waste water contaminated with VOCs, and compares favourably with steam stripping and carbon adsorption.

Pervaporation has been successfully adopted in the following applications:

- Pollution control of dilute solutions of hydrophobic solvents (e.g. 1000 ppm benzene in water)
- · Solvent recovery from process waste waters, and
- · Volume reduction of mixed-solvent hazardous waste

Pervaporation is particularly suited to waste water containing relatively hydrophobic volatile organics such as chlorinated solvents, naphthas, toluene and benzene.

Ultrafiltration, in which the effluent is passed across a semipermeable membrane at elevated pressures, may be used for the removal of organo-halogen and other pesticides. Efficiencies of removal of 95 to 99% have been achieved from effluent containing 500 to 5000 ug/l of total pesticides. After concentration the pesticides should be incinerated if recycling is not practicable.

Reverse osmosis is capable of removing hexachlorocyclohexane and malathion from waste waters at 99% efficiency.

Oxidation Techniques

Oxidation techniques may be particularly appropriate for difficult wastes for which biological treatment is not feasible. They could be associated with the process plant rather than a site system.

Wet Oxidation

For aqueous waste, wet air oxidation is generally more energy-efficient than incineration and is capable of oxidising complex molecules, including some pesticides, with up to 99.9% removal efficiencies. However, tests are normally required to confirm or otherwise the appropriateness of this technique.

Wet oxidation is the aqueous-phase oxidation of organic and inorganic compounds at elevated temperatures and pressures using compressed air, hydrogen peroxide or oxygen. In some systems additional catalysts are required. Temperatures between 100 and 300°C and pressures between 3 and 120 barg. are typically required, depending on which wet oxidation system is chosen and the characteristics of the waste being treated.

The oxidation stage can be used either to convert organics to carbon dioxide, water and nitrogen, or to break complex molecules down into simpler ones. The waste stream in the latter case will undergo a secondary treatment (e.g. biological) to complete the destruction.

The gaseous stream leaving the oxidation unit will sometimes need additional treatment to remove or destroy environmentally harmful compounds before release.

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There are some wet oxidation systems that are operated in the critical temperature and pressure region and can produce significant emissions of oxides of sulphur and oxides of nitrogen.

Advantages of wet oxidation include

- · emissions of nitrogen oxides are virtually eliminated where the oxidation temperature is low
- · emissions of dust or inorganic oxides are eliminated, and
- The oxidation is carried out in a closed system, which reduces the risk of release of unconverted material in the event of a process upset such as runaway reactions

Possible disadvantages include:

• A minimum concentration of oxidisable material is required to allow autothermal operation, and below this concentration an extra energy source is required.

Systems using water at supercritical conditions are largely in the demonstration and evaluation stage.

Advanced Oxidation Process

Strong oxidants such as hydrogen peroxide with a catalyst and ozone are used to oxidise organic compounds in waste waters to carbon dioxide, water, salts, etc. Promoting these free-radical reactions by use of ultraviolet light or semiconductor photocatalyst materials is termed advanced oxidation. Use of UV light and an oxidant is more commercially available than the photocatalyst route.

Consideration needs to be given to the effect of partial oxidation and whether resulting gaseous streams need further treatment. A pH higher than 9 should generally be avoided to prevent the potential formation of toxic phenolic substances.

Thermal Destruction

Non-biodegradable organic material can be treated by thermal incineration. However, the thermal destruction of mixed liquids can be highly inefficient and the waste should be dewatered prior to incineration.

Dissolved Material

Dissolved material, primarily inorganic salts, may not be removed at high efficiencies by the techniques described above. Dilution may occur in a site waste-water system and the Inspector should assess whether this is acceptable. Dissolved salts will be removed to some extent in conventional treatment systems such as flocculation and settling. Where specific abatement measures are needed, the options include:

- Chemical precipitation, although this may involve substitution of ions rather than removal
- Concentration by evaporation or membrane (see above) systems, with the concentrate passing to separate treatment
- · Crystallisation and recovery of solids, also applicable to some organic compounds
- · Ion exchange (see above) and recovery, and
- · Solvent extraction and recovery, particularly of organic material

In addition to the BREF and the techniques below, guidance on cost-effective effluent treatment techniques can be found in **Water efficiency references:**.

The primary consideration should be to prevent releases of harmful substances to the aquatic environment, whether releases are direct or via a sewage treatment works.

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Indicative BAT requirements for the control of effluent treatment

1

- The following general principles should be applied in sequence to control emissions to water:
 - water use should be minimised and wastewater reused or recycled (see Section 2.4.3)
- contamination risk of process or surface water should be minimised (see Section 2.2.5)
 - wherever possible, closed loop cooling systems should be used and procedures in place to ensure blow down is minimised
- where any potentially harmful materials are used measures should be taken to prevent them entering the water circuit
- 2 Consideration should be given to the use of filtration/osmosis or other techniques. such techniques allow the water to be cleaned to the above level for release or, preferably, be returned to the process. Particular consideration should be given to the fate of the concentrated residues of such techniques. These can often be returned to furnaces, evaporated, solidified, sent for incineration etc. that tankering of such residues off site as waste, simply transfers the problem to another place unless they are sent to a facility with the genuine ability to recycle the materials.
- 3 If the wastewater is all readily biodegradable or contains only materials which are naturally occurring in much larger quantities in the receiving water the Operator can offer justification as to why filtration/osmosis or other techniques are not appropriate.
- 4 Where prevention is not possible, the emissions benchmarks given in **Section 3**, are achievable.
- 5 Where effluent is treated off-site at a sewage treatment works the above factors apply in demonstrating that:
 - the treatment provided at the sewage treatment works is as good as would be achieved if the emission was treated on-site, based on reduction of load (not concentration) of each substance to the receiving water (using the IPPC Environmental Assessments for BAT software tool will assist in making this assessment).
 - action plans are appropriate in the event of sewer bypass, (via storm/emergency overflows
 or at intermediate sewage pumping stations) to prevent direct discharge of the waste waters
 during these periods, e.g. knowing when bypass is occurring, rescheduling activities such as
 cleaning or even shutting down when bypass is occurring.
 - a suitable monitoring programme is in place for emissions to sewer. This may be that specified by the sewerage undertaker to protect the treatment plant, or it may be more extensive if further controls are required to minimise the load released.
- 6 The Operator should maintain an understanding of the main chemical constituents of the treated effluent (including the make-up of the COD) and assessment of the fate of these chemicals in the environment.
- 7 All emissions should be controlled, as a minimum, to avoid a breach of water quality standards (see Section 3.2 and Section 4.1), but noting that where BAT can deliver further reduction at reasonable cost it should do so (see Section 1.1). Calculations and/or modelling to demonstrate this will be carried out in response to Section 4.1.

Raw

materials

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2.2.3 Point source emissions to groundwater

Groundwater protection legislation

Emission

control

The Groundwater Regulations for the UK came into force on 1 April 1999. If List I or List II substances (see Appendix 5) are discharged to groundwater or may be discharged to groundwater then the Environment Agency will provide advice as part of their statutory consultation duties.

- It shall not be granted at all if it would permit the direct discharge of a LIst I substance (Regulation 4 (1)) except in limited circumstances - see note 1, below.
- If the permit allows the disposal of a List I substance or any other activity that might lead to an indirect discharge (see note 2, below) of a List I substance then prior investigation (as defined in Regulation 7) is required and the Permit shall not be granted if this reveals that indirect discharges of List I substances would occur; in any event, conditions to secure the prevention of such discharges must be imposed (Regulation 4(2) and (3)).
- In the case of List II substances, Permits allowing direct discharges or possible indirect discharges, cannot be granted unless there has been a prior investigation and conditions must be imposed to prevent groundwater pollution (Regulation 5).
- The Regulations contain further detailed provisions covering surveillance of groundwater (Regulation 8); conditions required when direct discharges are permitted (Regulation 9); when indirect discharges are permitted (Regulation 10); and review periods and compliance (Regulation 11).

The principles, powers and responsibilities for groundwater protection in England and Wales, together with the Agency's policies on this, are outlined in the Environment Agency's document Policy and Practice for the Protection of Groundwater. This outlines the concepts of vulnerability and risk and the likely acceptability from the Agency's viewpoint of certain activities within groundwater protection zones. These are categorized as:

Prior investigation - of the potential effect on groundwater of on-site disposal activities discharges 1 to groundwater. Such investigations will vary from case to case, but the Regulator is likely to require a map of the proposed disposal area; a description of the underlying geology, hydrogeology and soil type, including the depth of saturated zone and quality of groundwater the proximity of the site to any surface waters and abstraction points, and the relationship between ground and surface waters; the composition and volume of waste to be disposed of; and the rate of planned disposal.

The Environment Agency has produced a series of maps of England and Wales, which provide a guide to potential groundwater vulnerability. Source Protection Zones are intended to aid protection by defining annular zones around each major potable source, including springs, boreholes and wells, based on travel times.

2 Surveillance - This will also vary from case to case, but will include monitoring of groundwater quality and ensuring the necessary precautions to prevent groundwater pollution are being undertaken.

Note 1	The Regulations state that, subject to certain conditions, the discharges of List I substances to groundwater may be authorised if the groundwater is "permanently unsuitable for other uses". Advice must be sought from the Regulator where this is being considered as a justification for such discharges.
Note 2	List I and List II refer to the list in the Groundwater Regulations and should not be confused with the similar lists in the Dangerous Substances Directive (see Appendix 3).

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Indicative BAT requirements for point source emissions to groundwater Identify if there may be a discharge of any List I or List II substances and if any are identified, explain how the requirements of the Groundwater Regulations 1998 have been addressed.

- 1 In general, there should be no permitted releases to groundwater of either a direct or indirect nature.
- 2 If such releases are to continue the requirements of the Regulations, as summarised above, must be complied with.

2.2.4 Control of fugitive emissions to air

Common sources of fugitive emissions are:

Fugitive VOC emissions are often a very significant factor in emissions to air from LVOC installations. Fugitive emissions of other substances such as sulphur and nitrogen compounds are referred to in the appropriate process descriptions in Section 2.3.1, together with the specialist techniques required to prevent them.

VOCs are often released through fugitive losses from sources including valves, flanges, pump seals and equipment vents. Due to the nature of such emissions, it is essential for them to be tackled through a structured programme of Leak detection and Reduction (LDAR) work. The principal areas of fugitive loss are well known and their minimising has been the subject of much investigation and subsequent improvement worldwide.

An essential first step of any programme is to establish a fugitive release inventory for the installation. This normally involves a combination of sampling, measurements, environmental monitoring, dispersion modelling and estimates based on emission factors. This is a major undertaking, which involves the following steps:

- Identifying all potential sources of VOC emissions, by establishing population counts of equipment components in line with up-to-date piping and instrumentation drawings for processes. This survey should cover gas, vapour and light liquid duties.
- Quantifying of the VOC emissions, initially as baseline estimates, and subsequently to more refined levels. Suitable protocols for this include the US EPA Method 21 for process component losses and API methods for tankage losses. Some major companies have developed their own techniques and protocols.
- Using appropriate dispersion modelling techniques, predict atmospheric mass flux and concentrations.
- Employing environmental monitoring techniques, compare the predicted situation with the measured one.

Installations should clearly tackle the largest losses first. In the case of process component fugitive emissions the best available technique, probably the only real option, is the implementation of a permanent on-going leak detection and repair (LDAR) programme. This should be developed and tailored to suit the situation concerned, using appropriate techniques, frequencies and priorities. It should provide estimates of fugitive VOC emissions for monitoring returns and enable action to be taken to minimise emissions.

LDAR programmes have been used successfully worldwide to reduce VOC emissions and are already in use in the UK. Typical survey results show that leaks from glands on valves and pumps are responsible for 90% or more of estimated fugitive emissions and that a small proportion of valves,

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virtually all on gas or high-temperature light material streams, contribute almost all of the total. Abatement of fugitive emissions is of particular importance for VOCs with a high environmental impact (Category A). Best available techniques used to minimise such process component fugitive emissions include the following:

- Use of low-emission valve stem packing (500 ppm) on critical valves, eg rising-stem gate-type control valves in continuous operation, particularly on gas/light liquid high-pressure/temperature duties.
- Use of alternative proven types of low-release valves where gate valves are not essential, e.g. quarter-turn and sleeved plug valves, both of which have two independent seals.
- Use of balanced bellows-type relief valves to minimise valve leakage outside of design lift range and piping of reliefs to flare, normally via phase separation, without header back-pressure.
- Minimising the number of flanged connections on pipelines and the use of high-specification jointing materials.
- · Use of canned pumps, magnetically driven pumps, or double seals on conventional pumps.
- Piping of compressor seals, vent and purge lines to flare systems.
- Use of end caps or plugs on open-ended lines and closed loop flush on liquid sampling points.
- Minimising the emissions to air from process hydrocarbon analysers, by optimising sampling volume/frequency and venting to flare systems.

As part of the Application the Operator will have identified and, where possible quantified, significant fugitive emissions to air from all relevant sources, estimating the proportion of total emissions that are attributable to fugitive releases for each substance. Where there are opportunities for reductions, the Permit may require the updated inventory of fugitive emissions to be submitted.

Indicative BAT requirements for fugitive emissions of VOCs and particulates to air (Sheet 1 of 2)

- 1 Dust The following general techniques should be employed where appropriate:
 - Covering of skips and vessels
 - Avoidance of outdoor or uncovered stockpiles (where possible)
 - Where unavoidable, use of sprays, binders, stockpile management techniques, windbreaks
 and so on
 - Regular wheel and road cleaning (avoiding transfer of pollution to water and wind blow)
 - Closed conveyors, pneumatic or screw conveying (noting the higher energy needs), minimising drops. Filters on the conveyors to clean the transport air prior to release
 - · Regular housekeeping
 - Enclosed silos (for storage of bulk powder materials) vented to fabric filters. The recycling of collected material should be considered under Section 2.6.
 - · Enclosed containers or sealed bags used for smaller quantities of fine materials

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Indicative BAT requirements for fugitive emissions of VOCs and particulates to air (Sheet 2 of 2)

- 2 VOCs
 - When transferring volatile liquids, the following techniques should be employed subsurface filling via filling pipes extended to the bottom of the container, the use of vapour balance lines that transfer the vapour from the container being filled to the one being emptied, or an enclosed system with extraction to suitable abatement plant.
 - Vent systems should be chosen to minimise breathing emissions (for example pressure/ vacuum valves) and, where relevant, should be fitted with knock-out pots and appropriate abatement equipment.
 - Maintenance of bulk storage temperatures as low as practicable, taking into account changes due to solar heating etc.
 - The following techniques should be used (together or in any combination) to reduce losses from storage tanks at atmospheric pressure:
 - Tank paint with low solar absorbency
 - Temperature control
 - Tank insulation
 - Inventory management
 - Floating roof tanks
 - Bladder roof tanks
 - Pressure/vacuum valves, where tanks are designed to withstand pressure fluctuations
 - Specific release treatment (such as adsorption condensation)
- 3 For Information on Odour, see Section 2.2.6.

2.2.5 Fugitive emissions to surface water, sewer and groundwater

Fugitive emissions, primarily from leaks and spillages, may occur into cooling water, site drainage water and groundwater. Their control must form part of a programme of good design, monitoring, maintenance and operating procedures. Aspects of these controls will be found in several parts of this Note, but they are brought together and summarised in this section.

Cooling Water

Leaks of process fluids into cooling water in heat exchangers are a frequent source of contamination. Monitoring of the cooling water at relevant points should be appropriate to the nature of the process fluids. In a recirculatory cooling system, leaks can be identified before significant emission to the environment has occurred. The potential for environmental impact is likely to be greater from a once through system. Planned maintenance can help to avoid such occurrences.

Site Drainage Water

Storage tanks and process vessels should be bunded. The bunding arrangements should be subject to risk assessment and be capable of containing at least 110% of the capacity of the largest tank within any one bund. Bunds should be impermeable and should have no direct connection to drains. The roofing of bunded areas can minimise the volume of potentially contaminated storm water. Bunds not frequently visited should be fitted with a high-level probe and an alarm as appropriate. Bunds should be regularly inspected for structural integrity by a competent person. The Environment Agency has issued guidance on tank storage.

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In addition to sealed bunds, possible measures to reduce contamination from large storage tanks include:

- · Double-walled tanks, and
- Leak detection channels.

Hard surfacing should be provided in areas where accidental spillage or leakage may occur, e.g. beneath prime movers, pumps, in storage areas, and in handling, loading and unloading areas. The surfacing should be impermeable to process liquors.

Hard surfacing of areas subject to potential contamination should be drained such that potentially contaminated surface run-off is not allowed to discharge to ground.

Stocks of suitable absorbents should be held at appropriate locations for use in mopping up minor leaks and spills, and should be disposed of to leak-proof containers.

Particular care should be taken in areas of inherent sensitivity to groundwater pollution. Poorly maintained drainage systems are in many cases known to be the main cause of groundwater contamination and surface/above-ground drains are preferred to facilitate leak detection (and to reduce explosion risks).

Additional measures could be justified in locations of particular environmental sensitivity. Decisions on the measures to be taken should take account of the risk to groundwater, taking into consideration the factors outlined in the Agency document, Policy and Practice for the Protection of Groundwater, including groundwater vulnerability and the presence of groundwater protection zones.

Groundwater Vulnerability

1

The vulnerability of groundwater to contaminants will depend on the natural characteristics of any given site, specifically on the physical, chemical and biological properties of soil and rocks beneath the site. The Environment Agency has produced a series of maps of England and Wales, which provide a guide to potential groundwater vulnerability. Source Protection Zones are intended to aid protection by defining annular zones around each major potable source, including springs, boreholes and wells, based on travel times.

Surveys of plant that may continue to contribute to leakage should also be considered, as part of an overall environmental management system. In particular, operators should consider undertaking leakage tests and/or integrity surveys to confirm the containment of underground drains and tanks.

As part of the Application the Operator will have identified and, where possible, quantified, significant fugitive emissions to water from all relevant sources, estimating the proportion of total emissions that is attributable to fugitive releases for each substance. Where there are opportunities for reductions, the Permit may require a regularly updated inventory of fugitive emissions to be submitted.

Indicative BAT requirements for fugitive emissions to water (Sheet 1 of 2)

- With regard to **subsurface structure**, the Operator should:
 - · establish and record the routing of all installation drains and subsurface pipework
 - · identify all subsurface sumps and storage vessels
 - engineer systems to minimise leakages from pipes and ensure swift detection if they do occur, particularly where hazardous (i.e. listed) substances are involved
 - provide, in particular, secondary containment and/or leakage detection for such subsurface pipework, sumps and storage vessels
 - establish an inspection and maintenance programme for all subsurface structures, e.g. pressure tests, leak tests, material thickness checks or CCTV

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Indicative BAT requirements for fugitive emissions to water (Sheet 2 of 2)

- 2 For surfacing, the Operator should:
 - describe the design and condition of the surfacing of all operational areas (Relevant information may include as appropriate: capacities; thicknesses; falls; material; permeability; strength/reinforcement; resistance to chemical attack; inspection and maintenance procedures; and quality assurance procedures.)
 - have an inspection and maintenance programme of impervious surfaces and containment kerbs
 - justify where operational areas have not been equipped with:
 - an impervious surface
 - spill containment kerbs
 - sealed construction joints
 - connection to a sealed drainage system
- 3 All tanks containing liquids whose spillage could be harmful to the environment should be bunded. For further information on bund sizing and design, see the Releases to water references. Bunds should:
 - · be impermeable and resistant to the stored materials
 - · have no outlet (that is, no drains or taps) and drain to a blind collection point
 - · have pipework routed within bunded areas with no penetration of contained surfaces
 - · be designed to catch leaks from tanks or fittings
 - have a capacity greater than 110 percent of the largest tank or 25 percent of the total tankage
 - be subject to regular visual inspection and any contents pumped out or otherwise removed under manual control after checking for contamination
 - · where not frequently inspected, be fitted with a high-level probe and an alarm as appropriate
 - · have fill points within the bund where possible or otherwise provide adequate containment
 - have a routine programmed inspection of bunds (normally visual, but extending to water testing where structural integrity is in doubt)
- 4 All sumps should:
 - · be impermeable and resistant to stored materials
 - be subject to at least 6-monthly visual inspection and any contents pumped out or otherwise removed after checking for contamination
- 5 Storage areas and containers should be designed and operated to minimise the risk of releases to the environment. In particular:
 - Storage areas should be located away from watercourses and sensitive boundaries, for example, adjacent to areas of public use, and should be protected against vandalism.
 - Storage areas should be clearly marked and signed plus containers should be clearly labelled.
 - The maximum storage capacity of storage areas should be stated and not exceeded. The maximum storage period for containers should be specified.
 - Appropriate storage facilities should be provided for special requirements such as for substances that are flammable, sensitive to heat or light and the like; also incompatible waste types should be kept separate.
 - Containers should be stored with lids, caps and valves secured and in place. This also applies to emptied containers.
 - Storage containers, drums and the like should be inspected at least once a week.

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2.2.6 Odour

Many of the substances used in the processes in this industrial sector have some potential to cause odour, but the odour threshold of the substances differs widely. Information is given in the Research Report RR/95/009, the Categorisation of Volatile Organic Compounds. Generally, compounds of sulphur such as mercaptans and thiols, nitrogen compounds such as amines, acrylates and some organic acids are particularly pungent.

The generic BATs for preventing planned and fugitive emissions to air included in Section 2.2.1 and Section 2.2.4 . are the basis for odour prevention from the process. In the case of processes handling highly odorous materials, it is necessary to use the strictest techniques to prevent trace emissions. These are included as special techniques in the descriptions of the relevant processes in Section 2.2.

Odorous compounds can be emitted from the treatment of otherwise innocuous substances, for example in the biological treatment of waste water. Incorrectly designed or operated facilities intended to be aerobic may not provide sufficient aeration and may allow the formation of odorous compounds in anaerobic conditions. Volatile compounds may be released on first exposure of the waste water to the atmosphere. Their emission may need to be prevented by covering the tank or separator and recovering the compounds.

The level of detail supplied should be in keeping with the risk of causing odour-related annoyance at sensitive receptors.

Where an installation poses no risk of odour-related environmental impact because the activities undertaken are inherently non-odorous, this should be justified and no further information relating to odour need normally be supplied.

Where odour could be a problem, the Operator will be required in the Application to supply the information as indicated below:

- Information relating to sensitive receptors, in particular the type of receptor, location relative to the odour sources and an assessment of the impact of odorous emissions on the receptors. Where detailed information is required the Operator may be able to secure an agreement to supply this as part of an Improvement Programme.
- An overview of any complaints received, what they relate to (source/operation) and remedial action taken.
- The types and source of odorous substances used or generated, intentional and fugitive (unintentional) release points and monitoring undertaken.
- Actions taken to prevent or minimise
 - A description of the actions taken to prevent and/or minimise odour annoyance for each odour source.
 - A demonstration that the indicative BAT requirements are being complied with.
 - Identification of any circumstances or conditions which might compromise the ability to prevent or minimise odour annoyance, and a description of the actions that will be taken to minimise the impact.

There may be a requirement placed upon the Operator to provide some or all of this information in the form of an odour management statement. See the Odour management statement for a typical log book.

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Indicative BAT requirements for odour control

- 1 The requirements for odour control will be installation-specific and depend on the sources and nature of the potential odour. In general:
- 2 Where odour can be contained, for example within buildings, the Operator should maintain the containment and manage the operations to prevent its release at all times.
- 3 Where odour releases are expected to be acknowledged in the Permit, (i.e. contained and treated prior to discharge or discharged for atmospheric dispersion):
 - For existing installations, the releases should be modelled to demonstrate the odour impact at sensitive receptors. The target should be to minimise the frequency of exposure to ground level concentrations that are likely to cause annoyance.
 - For new installations, or for significant changes, the releases should be modelled and it is expected that the Operator will achieve the highest level of protection that is achievable with BAT from the outset.
 - Where there is no history of odour problems then modelling may not be required although it should be remembered that there can still be an underlying level of annoyance without complaints being made.
 - Where, despite all reasonable steps in the design of the plant, extreme weather or other incidents are liable, in the view of the Regulator, to increase the odour impact at receptors, the Operator should take appropriate and timely action, as agreed with the Regulator, to prevent further annoyance (these agreed actions will be defined either in the Permit or in an odour management statement).
- 4 Where odour generating activities take place in the open, (or potentially odorous materials are stored outside) a high level of management control and use of best practice will be expected.
- 5 Where an installation releases odours but has a low environmental impact by virtue of its remoteness from sensitive receptors, it is expected that the Operator will work towards achieving the standards described in this Note, but the timescales allowed to achieve this might be adjusted according to the perceived risk.

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2.3 Management

Within IPPC, an effective system of management is a key technique for ensuring that all appropriate pollution prevention and control techniques are delivered reliably and on an integrated basis.

The Regulators strongly support the operation of environmental management systems (EMSs). An Operator with such a system will find it easier to complete not only this section but also the technical/ regulatory requirements in the following sections

The Regulators recommend either certification to the ISO 14001 standard or registration under EMAS (EC Eco Management and Audit Scheme) (OJ L114, 24/04/01). Both certification and registration provide independent verification that the EMS conforms to an assessable standard. EMAS now incorporates ISO 14001 as the specification for the EMS element. We believe that EMAS has a number of benefits over ISO14001 including a greater focus on environmental performance; a greater emphasis on legal compliance; and a public environmental statement. For further details about ISO 14001 and EMAS contact British Standards Institute (BSI) and the Institute of Environmental Management and Assessment (IEMA) respectively.

An effective EMS will help the Operator to maintain compliance with regulatory requirements and to manage other significant environmental impacts. This section identifies only those EMS requirements that are not specifically covered elsewhere in other sections of the document. It should not, therefore, be taken to describe all of the elements of an effective environmental management system. While the requirements below are considered to be BAT for IPPC, they are the same techniques as required in a formal EMS and are also capable of delivering wider environmental benefits. However, it is information on their applicability to IPPC which is primarily required in this application.

Indicative BAT requirements for management techniques (Sheet 1 of 3)

Operations and maintenance

- 6 Effective operational and maintenance systems should be employed on all aspects of the process whose failure could impact on the environment, in particular there should be:
 - documented procedures to control operations that may have an adverse impact on the environment
 - a defined procedure for identifying, reviewing and prioritising items of plant for which a preventative maintenance regime is appropriate
 - documented procedures for monitoring emissions or impacts
 - a preventative maintenance programme covering all plant, whose failure could lead to impact on the environment, including regular inspection of major 'non productive' items such as tanks, pipework, retaining walls, bunds ducts and filters
- 7 The maintenance system should include auditing of performance against requirements arising from the above and reporting the result of audits to top management.

Competence and training

- 8 Training systems, covering the following items, should be in place for all relevant staff which cover
 - awareness of the regulatory implications of the Permit for the activity and their work activities;
 - awareness of all potential environmental effects from operation under normal and abnormal circumstances
 - · awareness of the need to report deviation from the Permit
 - · prevention of accidental emissions and action to be taken when accidental emissions occur

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Indicative BAT requirements for management techniques (Sheet 2 of 3)

- 9 The skills and competencies necessary for key posts should be documented and records of training needs and training received for these post maintained.
- 10 The key posts should include contractors and those purchasing equipment and materials;
- 11 The potential environmental risks posed by the work of contractors should be assessed and instructions provided to contractors about protecting the environment while working on site.
- 12 Where industry standards or codes of practice for training exist (e.g. WAMITAB) they should be complied with.

Accidents/incidents/non conformance

- 13 There should be an accident plan as described in Section 2.8 which:
 - · identifies the likelihood and consequence of accidents
 - · identifies actions to prevent accidents and mitigate any consequences
- 14 There should be written procedures for handling, investigating, communicating and reporting actual or potential non-compliance with operating procedures or emission limits.
- 15 There should be written procedures for handling, investigating, communicating and reporting environmental complaints and implementation of appropriate actions.
- 16 There should be written procedures for investigating incidents, (and near misses) including identifying suitable corrective action and following up

Organisation

- 17 The following are indicators of good performance which will impact on Agency resources, but upon which we will not normally insist as Permit conditions
- 18 The company should preferably adopt an environmental policy and programme which:
 - · includes a commitment to continual improvement and prevention of pollution
 - includes a commitment to comply with relevant legislation, and with other requirements to which the organisation subscribes
 - identifies, sets, monitors and reviews environmental objectives and key performance indicators independently of the Permit
- 19 The company should preferably have procedures which incorporate environmental issues into the following areas (as supported by demonstrable evidence e.g. written procedures):
 - · the control of process change on the installation
 - design and review of new facilities (including provision for their decommissioning), engineering and other capital projects
 - · capital approval
 - · purchasing policy
- 20 The company should preferably have audits, at least annually, to check that all activities are being carried out in conformity with the above requirements. These should preferably be independent.
- 21 The company should preferably report annually on environmental performance, objectives and targets, and future planned improvements. This should preferably be a public environmental statement.
- 22 The company should preferably have a registered or certified EMAS/ISO 14001 system (by an accredited certification body)

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Indicative BAT requirements for management techniques (Sheet 3 of 3)

23 The company should preferably have a clear, logical and recorded system for keeping records of:

policies

- · roles and responsibilities
- targets
- procedures
- · results of audits
- · results of reviews

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2.4 Raw Materials

disposal

This section covers the use of raw materials and water and the techniques for both minimising their use and minimising their impact by selection. (Energy and fuels are covered under Section 2.7, Energy).

As a general principle, the Operator will need to demonstrate the measures taken to:

- reduce the use of chemicals and other materials (Section 2.4.2)
- substitute less harmful materials, or those which can be more readily abated and when abated lead to substances that are more readily dealt with
- understand the fate of by-products and contaminants and their environmental impac (Section 2.4.2)

2.4.1 Raw materials selection

This section looks at the selection and substitution of raw materials and Section 2.4.2 describes the techniques to minimise their use.

It should be recognised that the process of selecting raw materials can present an opportunity to control emissions at source. In this regard it is suggested that Operators closely examine the range of possible raw material options available to them.

The Application requires the Operator to supply a list of the materials used, which have the potential for significant environmental impact, including:

- the chemical composition of the materials where relevant
- the quantities used
- the fate of the material (i.e. approximate percentages to each media and to the product)
- environmental impact where known (for example. degradability, bioaccumulation potential, toxicity to relevant species)
- any reasonably practicable alternative raw materials that may have a lower environmental impact including, but not limited to any alternatives described in the BAT requirements below (the substitution principle)
- and to justify (for example, on the basis of impact on product quality) the continued use of any substance for which there is a less hazardous alternative to show that the proposed raw materials are therefore BAT.

What raw material selection is often determined in the first instance by the design of the process. To manufacture a particular obtaining a product, there is sometimes a choice between processes which use raw materials of different potential for environmental harm, which have different product yields, which generate different types or amount of wastes. Generally the process with the least environmental impact should be chosen, although it should be recognised that the choice may be constrained, for example by the integration of the process in a complex site.

The purity of raw materials will often affect yields and the presence of impurities may result in the need for excessive recycle and/or recovery operations with consequent higher energy consumption. The use of high purity raw materials will generally minimise the environmental impact of that process but may have adverse consequences on their own upstream production. The use of oxygen rather than air in oxidation processes is an example where the oxidation benefits have to be weighed against the energy requirements for air separation.

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The use of catalysts can result in large improvements in reaction selectivity and conversion rates, resulting in lower waste formation and energy usage. Reactions often proceed at lower temperatures and pressures when catalysed. The development of new and improved catalysts is important in many sectors of the industry. In addition to their use in new processes, they can sometimes be retrofitted to improve the environmental and economic performance of existing installations. The activity of some improved catalysts is so high that it may be unnecessary to remove them from the product, for example in some polyolefin production. The activity of fixed catalysts usually declines with time and they may need regeneration or replacement. Some catalysts are toxic and it is necessary to control their dispersion, recovery and reuse or disposal. The least polluting catalyst should be selected where a choice exists.

Solvents vary widely in their environmentally harmful properties, for example, in toxicity, stratospheric ozone depletion potential (ODP), photochemical ozone creation potential (POCP) and in their contribution to global climate change. Where possible, they should be selected to be of low environmental impact.

The use of gaseous fuels rather than heavy fuel oils is generally to be preferred as they are more easily desulphurised, the formation of nitrogen oxides in combustion equipment is more easily reduced and there is less tendency for fouling. The choice of fuel may be influenced by the overall availability of fuel gas on a large site such as a petroleum refinery or petrochemical complex.

Indicative BAT requirements for raw materials selection

- 1 The Operator should maintain the list of materials referred to above.
- 2 The Operator should have procedures for the regular review of new developments in raw materials and the implementation of any suitable ones with an improved environmental profile.
- 3 The Operator should have quality-assurance procedures for controlling the content of raw materials.
- 4 The Operator should complete any longer-term studies needed into the less polluting options and should make any material substitutions identified

2.4.2 Waste minimisation audit (minimising the use of raw materials)

The options for waste recovery and recycling are covered in **Section 2.6**. Waste avoidance/ minimisation, and the use of clean technologies, is a theme which runs throughout **Section 2.1** and **Section 2.2**. This section deals with the systematic approach to look for other opportunities.

Waste minimisation can be defined simply as: "a systematic approach to the reduction of waste at source, by understanding and changing processes and activities to prevent and reduce waste".

A variety of techniques can be classified under the term waste minimisation, from basic housekeeping through statistical measurement, to application of clean technologies.

In the context of waste minimisation and this Guidance, waste relates to the inefficient use of raw materials and other substances at an installation. A consequence of waste minimisation will be the reduction of gaseous, liquid and solid emissions.

Key operational features of waste minimisation will be:

- the ongoing identification and implementation of waste prevention opportunities
- the active participation and commitment of staff at all levels including, for example staff suggestion schemes
- · monitoring of materials' usage and reporting against key performance measures

For the primary inputs to waste activities e.g. incineration, the requirements of this section may have been met "upstream" of the installation. However, there may still be arisings that are relevant.

See the **Waste minimisation support references** for detailed information, guides and case studies on waste minimisation techniques.

Indicative BAT requirements for waste minimisation audits Identify the raw and auxiliary materials, other other substances that are proposed for use.

- 1 The Operator should carry out a waste minimisation audit at least every 4 years. If an audit has not been carried out in the 2 years prior to submission of the application and the details made known at the time of the application, then the first audit shall take place within 2 years of the issue of the Permit. The methodology used and an action plan for reducing the use of raw materials should be submitted to the Regulator within 2 months of completion of the audit. The audit should be carried out as follows:
- 2 The Operator should analyse the use of raw materials, assess the opportunities for reductions and provide an action plan for improvements using the following three essential steps
 - process mapping
 - materials mass balance
 - action plan
- 3 The use and fate of raw materials and other materials, including by-products, solvents and other support materials, such as fuels, catalysts and abatement agents, should be mapped onto a process flow diagram (see the Waste minimisation support references). This should be achieved by using data from the raw materials inventory and other company data as appropriate. Data should be incorporated for each principal stage of the operation in order to construct a mass balance for the installation.
- 4 Using this information, opportunities for improved efficiency, changes in process and waste reduction should be generated and assessed. An action plan should then be prepared for implementing improvements to a timescale approved by the Regulator.

2.4.3 Water use

Water is used in LVOC processes for cooling, process use and for cleaning.

Where water is needed for cooling, its use should first be minimised by maximising heat transfer between process streams is also more energy efficient. Water should normally be used in recirculating systems with indirect heat exchangers and a cooling tower rather than a once through system. This avoids most of the heat transfer to the aquatic environment and reduces risks of undetected contamination. The quantity of treatment chemicals required is likely to be reduced. However, a water make-up treatment plant and a concentrated purge stream from the system are likely to be necessary. Where water is used in a once through cooling system, additional precautions and treatment will be required to minimise the risk of emissions of pollutants to the receiving of water.

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Air cooling can be used in place of water where the characteristics of the process permit, but it uses energy in the fans and may be noisy in operation.

In the choice and design of cooling systems, it should be noted that the efficiency of cooling can have a significant effect on the release of uncondensed VOCs. An increase of a few degrees in condensation temperature may result in a multiple increase in VOC emissions. This subject is treated in detail in the Cooling BREF (Reference 1).

Water may be used in direct contact with process materials for either scrubbing or quench cooling. In most cases the water can be recirculated after stripping out the absorbed substances. A purge stream is normally required to avoid the build-up of contaminants and to remove water that is produced in the process. This will need treatment before discharge, although in some cases it may be used in another process, for example ethylene oxide and glycol processes.

Water used for cleaning can be reduced by a number of techniques, e.g. by using dry methods where possible and spray cleaning rather than whole vessel filling. Water should be reused wherever possible and a hierarchy of sources and opportunities for reuse may be established using pinch analysis.

Reasons for reducing water use

Water use should be minimised within the BAT criteria for the prevention or reduction of emissions and be commensurate with the prudent use of water as a natural resource.

Reducing water use may be a valid environmental (or economic) aim in itself, perhaps because of local supply constraints. Also, from the point of view of reducing polluting emissions, any water passing through an industrial process is degraded by the addition of pollutants, and there are distinct benefits to be gained from reducing the water used. These include:

- reducing the size of (a new) treatment plant, thereby supporting the cost benefit BAT justification of better treatment
- · cost savings where water is purchased or disposed of to another party
- associated benefits within the process such as reduced energy requirements for heating and pumping, and reduced dissolution of pollutants into the water leading to reduced sludge generation in the effluent treatment plant

The use of a simple mass balance for water use may help to reveal where reductions can be made.

Advice on cost-effective measures for minimising water can be found in the **Water efficiency** references:

Indicative BAT requirements for minimisation of water use (Sheet 1 of 2)

- 1 The Operator should carry out a regular review of water use (water efficiency audit) at least every 4 years. If an audit has not been carried out in the 2 years prior to submission of the application and the details made known at the time of the application, then the first audit shall take place within 2 years of the issue of the Permit. The methodology used and an action plan for reducing the use of raw materials should be submitted to the Regulator within 2 months of completion of the audit.
 - The Operator should produce flow diagrams and water mass balances for the activities.
 - Water-efficiency objectives should be established by comparison with the benchmarks above. In justifying any departures from these, or where benchmarks are not appropriate, the techniques described below should be taken into account. The constraints on reducing water use beyond a certain level should be identified by each Operator, as this is usually installation-specific.
 - Water pinch techniques should be used in the more complex situations, particularly on chemical plant, to identify the opportunities for maximising reuse and minimising use of water (see the Water efficiency references:).

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Indicative BAT requirements for minimisation of water use (Sheet 2 of 2)

- 2 Using this information, opportunities for reducing water use should be generated and assessed. An action plan should then be prepared implementing improvements to a timescale approved by the Regulator.
- 3 The following general principles should be applied in sequence to reduce emissions to water:
 - water-efficient techniques should be used at source where possible
 - water should be recycled within the process from which it issues, by treating it first if necessary. Where this is not practicable, it should be recycled to another part of the process that has a lower water-quality requirement
 - in particular, uncontaminated roof and surface water, which cannot be used, should not be mixed with contaminated water until the latter has been treated in the effluent treatment system and after final monitoring
- 4 Measures should be implemented to minimise contamination risk of process or surface water (see Section 2.2.5).
- 5 To identify the scope for substituting water from recycled sources, the water-quality requirements associated with each use should be identified. Less contaminated water streams, such as cooling waters, should be kept separate where there is scope for reuse, possibly after some form of treatment.
- 6 Ultimately wastewater will need some form of treatment (see Section 2.2.2). However in many applications, the best conventional effluent treatment produces a good water quality that may be usable in the process directly or when mixed with fresh water. While treated effluent quality can vary, it can be recycled selectively, when the quality is adequate, reverting to discharge when the quality falls below that which the system can tolerate. The Operator should identify where treated water from the effluent treatment plant could be used and justify where it is not.
- 7 In particular, the cost of membrane technology continues to reduce. They can be applied to individual process streams or to the final effluent from the effluent treatment plant. Ultimately, they could completely replace the ETP plant, leading to greatly reduced effluent volume. There remains, however, a concentrated effluent stream but, where this is sufficiently small, and particularly where waste heat is available for further treatment by evaporation a zero effluent system could be produced. Where appropriate, the Operator should assess the costs and benefits of providing such treatment.
- 8 Water used in cleaning and washing down should be minimised by:
 - · vacuuming, scraping or mopping in preference to hosing down
 - · evaluating the scope for reusing wash water
 - · trigger controls on all hoses, hand lances and washing equipment
- 9 Fresh water consumption should be directly measured and recorded regularly ideally on a daily basis.

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2.5 Waste Handling

The normal nature and source of the waste from each activity is given in **Section 2.4.2** and will be confirmed in detail in the Operator's response to the emissions inventory.

2.5.1 Nature of Sector Wastes

The wastes produced by the sector are specific to the individual processes and are included in the process descriptions in section 2.1. They can be classified into types as follows:

- by-products for which no internal use or external sale is available
- residues from separation processes such as distillation
- · catalysts which have declined in performance and require replacement
- · filter cake, activated carbon, ion exchange resins, molecular sieves and other treatment materials
- sludges from waste water treatment
- · emptied containers and packaging
- maintenance and construction materials

The key pollutants likely to be present can be derived from knowledge of the process, materials of construction, corrosion/erosion mechanisms and materials related to maintenance, validated as necessary by the appropriate analytical techniques. The presence of substances created by abnormal operation should be identified, since process abnormalities can carry through substances into the waste that are not normally present.

2.5.2 Handling and Storage of Wastes

A system should be maintained to record the quantity, nature, origin and where relevant, the destination, frequency of collection, mode of transport and treatment method of any waste which is disposed of or recovered. Records must be maintained of any waste sent off-site (Duty of Care).

All substances produced by the process and disposed of to land on or away from the site should be handled and conveyed so as to prevent spillage, dust release or the generation of odours.

Wherever practicable, waste should be segregated and the disposal route identified which should be as close to the point of production as possible. Dedicated storage areas should be located away from watercourses and sensitive boundaries e.g. adjacent to areas of public use and protected against vandalism. Methods to prevent cross-contamination of wastes and the mixing of incompatible materials should be implemented. Storage areas should be clearly marked and containers should be clearly labelled. The maximum storage capacity of storage areas should be stated and not exceeded. The maximum storage period for containers should be specified.

Liquids and sludges should be stored in tanks, sealed or covered containers in a secure bunded area pending disposal. Where spillage could occur the plant layout should be such that any spillage can be collected and cannot enter any drainage system.

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Appropriate storage facilities should be provided for special requirements such as for substances which are flammable, sensitive to heat or light etc., and incompatible waste types should be kept separate. Storage of wastes of particular environmental sensitivity, such as halogenated organics, should be avoided as far as possible unless the materials are fixed or otherwise rendered harmless. Storage containers, drums etc. should be regularly inspected and procedures should be in place to deal with damaged or leaking containers.

Indicative BAT requirements for waste handling

Characterise and quantify each waste stream and describe the proposed measures for waste management, storage and handling.

- 1 A system should be maintained to record the quantity, nature, origin and, where relevant, the destination, frequency of collection, mode of transport and treatment method of any waste that is disposed of or recovered.
- 2 Wherever practicable, waste should be segregated and the disposal route identified. This should be as close to the point of production as possible.
- 3 Records should be maintained of any waste sent off-site (Duty of Care).
- 4 All appropriate steps to prevent emissions (for example, liquids, dust, VOCs and odour) from storage or handling should be taken (see Section 2.2.4, Section 2.2.5 and Section 2.2.6).

or disposal

In-process controls

Emissions controls

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Waste

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2.6 Waste recovery or disposal

Energy

The Regulations require the Regulator, in setting Permit conditions, to take account of certain general principles, including that the installation in guestion should be operated in such a way that "waste production is avoided in accordance with Council Directive 75/442/EEC on waste; and where waste is produced it is recovered, or where this is technically or economically impossible it is disposed of, while avoiding or reducing the impact on the environment". The objectives of the National Waste Strategies should also be considered. Waste avoidance (minimisation) is covered throughout Section 2.1 and Section 2.2. and by the specific requirement for a waste minimisation audit in Section 2.4.2.

To meet this requirement, the Regulator needs Operators to provide the information in point 2 below.

All wastes should be reviewed against this approach as there are opportunities and problems particular to each process. Some disposal options for particular processes are indicated in Section 2.1., but some generic sectoral conclusions can be drawn.

Waste minimisation is addressed in other sections of this Note and there are reference documents produced by e.g. the Institution of Chemical Engineers. Minimisation begins with the choice of process chemistry to give the optimum stoichiometry. Catalysts can often increase the product yield by improving conversion and selectivity.

Wastes can sometimes be recycled into the process or may be used in another process either within the installation or sold to another company for use. For example, waste solvent may not be pure enough for direct reuse but may be satisfactory for a less demanding process. Such outlets may justify expenditure to extract further useful materials from distillation residues and mixed fractions. Waste exchanges and Trade Associations may be helpful in locating productive outlets.

Scrubbing liquids such as ethanolamines are usually recovered and recycled on site, but may require further treatment if they become degraded. Recovery, if necessary by the supplier, is preferred to destruction.

The use of catalysts in this sector is particularly significant. Some can be regenerated in place but many need removal and replacement. Many are based on precious metals and it is economic to recover these, usually by return to the supplier. Every effort should be made to recycle other catalysts even where the economics are less attractive.

Many organic wastes have a useful thermal value and this can be realised by burning under controlled conditions. Waste hydrocarbon gases are commonly used as fuel and it is preferred to remove pollutants such as sulphur compounds before combustion. Other waste gases such as hydrogen cyanide, if not sold, are best combusted on site under conditions appropriate to their hazardous nature.

Whilst the occasional flaring of gaseous wastes may be essential for safety purposes, it does not provide good control of combustion. It does not allow recovery of heat nor abatement of polluting emissions. Flaring should not be a preferred method of routine disposal of gaseous wastes. See Section 2.2.1 . for further details.

Where recovery or chemical treatment of liquid wastes is not feasible, thermal destruction is the next preferred alternative. This may involve one of the oxidation techniques outlined in Section 2.2.5. of which incineration is the most common. A correctly designed and operated incinerator ensures a high degree of controlled combustion, allows recovery of heat and abatement of polluting emissions which may be formed. For example, halogenated wastes need to be destroyed under hazardous waste incineration conditions with scrubbing of the flue gases to remove acid pollutants. They should not be disposed to land.

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Landfill may be suitable for a limited number of wastes which are non polluting or are solidified or encapsulated to prevent release of contaminants. For example, some metal compounds when treated with lime are highly insoluble. Landfill of wastes from this sector should only be contemplated after all other alternatives have been thoroughly examined and rejected.

Indicative BAT requirements for waste recovery or disposal Describe and justify how each waste stream is proposed to be disposed of.

- 1 Waste should be recovered, unless it is technically or economically impossible to do so.
- 2 Where waste must be disposed of, unless agreed with the Regulator to be inappropriate, the Operator should provide a detailed assessment identifying the best environmental options for waste disposal. For existing activities, this may be carried out as an improvement condition to a timescale to be approved by the Regulator.

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2.7 Energy

BAT for energy efficiency under the PPC Regulations will be satisfied provided the Operator meets the following conditions:

either

the Operator meets the basic energy requirements in Section 2.7.1 and Section 2.7.2 below and is a
participant to a Climate Change Agreement (CCA) or a Direct Participant Agreement (DPA) within
the Emissions Trading Scheme.

or

the Operator meets the basic energy requirements in Section 2.7.1 and Section 2.7.2 below and the further sector-specific energy requirements in Section 2.7.3 below.

Note that even where a Climate Change Agreement or Direct Participant Agreement is in place, this does not preclude the consideration of energy efficiency (including those identified in Section 2.7.3) as part of an integrated assessment of BAT where they impact on other emissions, e.g. where:

- · the choice of fuel impacts upon emissions other than carbon, e.g. sulphur in fuel
- the minimisation of waste by waste-to-energy does not maximise energy efficiency, e.g. by Combined Heat and Power (CHP)
- the most energy-intensive abatement leads to the greatest reduction in other emissions

Further guidance is given in the guidance note H2 Energy efficiency for IPPC.

2.7.1 Basic energy requirements (1)

The requirements of this section are basic, low cost, energy standards that apply whether or not a CCA or DPA is in force for the installation.

Indicative BAT requirements for basic energy requirements (1): Provide a breakdown of the energy consumption and generation by source and the associated

environmental emissions.

- 1 The Operator should provide annually the energy consumption information, shown in the table below, in terms of delivered energy and also, in the case of electricity, converted to primary energy consumption. For the public electricity supply, a conversion factor of 2.6 should be used. Where applicable, the use of factors derived from on-site heat and/or power generation, or from direct (non-grid) suppliers should be used. In the latter cases, the Operator should provide details of such factors. Where energy is exported from the installation, the Operator should also provide this information. In the application this information should be submitted in the inventory in the H1 software tool and should also supplement this with energy flow information (such as "Sankey" diagrams or energy balances) showing how the energy is used throughout the process.
- 2 The Operator should provide the following Specific Energy Consumption (SEC) information. Define and calculate the SEC of the activity (or activities) based on primary energy consumption for the products or raw material inputs that most closely match the main purpose or production capacity of the installation. Provide a comparison of SEC against any relevant benchmarks available for the sector.

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Indicative BAT requirements for basic energy requirements (1): Provide a breakdown of the energy consumption and generation by source and the associated environmental emissions.

3 The Operator should provide associated environmental emissions. This is dealt with in the Operator's response to the emissions inventory using the H1 software tool.

Table 2.1: Example breakdown of delivered and primary energy consumption

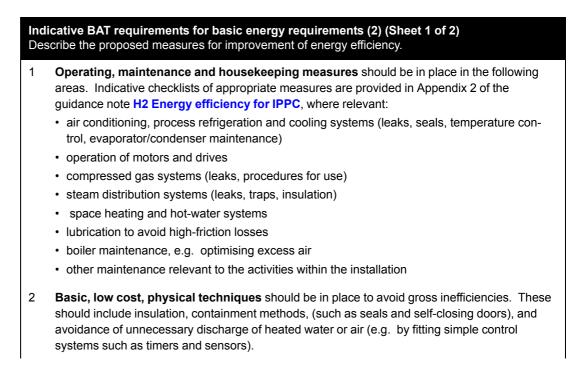
Energy source	Energy consumption		
	Delivered, MWh	Primary, MWh	% of total
Electricity*			
Gas			
Oil			
Other (Operator to specify)			

* specify source.

* specify source.

2.7.2 Basic energy requirements (2)

The requirements of this section are basic, low-cost, energy standards that apply whether or not a CCA or DPA is in force for the installation.



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Indicative BAT requirements for basic energy requirements (2) (Sheet 2 of 2) Describe the proposed measures for improvement of energy efficiency.

- 3 Energy-efficient building services should be in place to deliver the requirements of the Building Services section of the guidance note H2 Energy efficiency for IPPC. For energyintensive industries these issues may be of minor impact and should not distract effort from the major energy issues. They should nonetheless find a place in the programme, particularly where they constitute more than 5 percent of the total energy consumption.
- 4 **Energy management techniques** should be in place, according to the requirements of Section 2.3 noting, in particular, the need for monitoring of energy flows and targeting of areas for reductions.
- 5 An energy efficiency plan should be provided that:
 - identifies all techniques relevant to the installation, including those listed above and in Section 2.7.3, that are applicable to the installation
 - estimates the CO₂ savings that would be achieved by each measure over its lifetime
 - and, in the case where the activities are NOT covered by a CCA or DPA; provides information on the equivalent annual costs of implementation of the technique, the costs per tonne of CO₂ saved and the priority for implementation. A procedure is given in the Energy Efficiency Guidance Note.
- 6 An example format of the energy efficiency plan is shown in Table 2.2.

Table 2.2: Example format for energy efficiency plan

ALL APPLICANTS			ONLY APPLICANTS V	VITHOUT CCA	
Energy efficiency measure	CO ₂ savings	(tonnes)	Equivalent	EAC/CO ₂ saved	Date for imple- mentation
measure	Annual	lifetime	Annual Cost (EAC) £k	£/tonne	mentation

Refer to Energy Efficiency Guidance Note for appraisal methodology. Where other appraisal methodologies have been used, state the method, and provide evidence that appropriate discount rates, asset life and expenditure (\pounds/t) criteria have been employed.

The energy efficiency plan is required to ensure that the Operator has considered all relevant techniques. However, where a CCA or DPA is in place the Regulator will only enforce implementation of those measures in categories 1-3 above.

2.7.3 Further energy-efficiency requirements

LVOC processes are often large users of heat and power and some produce heat from their exothermal reactions. There may thus be greater opportunities for optimising energy efficiency in comparison with some other industrial processes.

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Combined heat and power plants are widely used in the sector and can dramatically improve the overall thermal efficiency of an installation. The availability of fuel gas coupled with a large demand for both power for duties such as compressors and pumps and heat for processing makes them especially attractive.

Cracking furnaces and other fired process heaters operate at high temperatures and optimum design can significantly improve thermal efficiency. Some older heaters operate at relatively low thermal efficiencies and upgrading or replacement may be justified by efficiency improvements before their expected date for replacement. Additional heat transfer within the heater and recovery of heat from flue gases may be practicable.

There are many opportunities for heat exchange between process streams. These are often already exploited in existing installations, but there may be scope for extending the exchange of heat. In process design, the maximum extent of internal heat exchange should be used in preference to the use of external heat and cooling utilities. This has incentives in both operating costs and environmental performance. Pinch analysis may be profitably used to determine the best alternative design.

Pumps and compressors are sometimes required to run at part load and techniques such as throttling and bypassing can be inefficient. The use of drives such as variable speed electric motors may be more efficient. Where there are technical problems in operating equipment such as gas turbines at reduced speeds, it may be preferable to install more than one set and to shut down one or more when loads are low.

It may be possible to recover power from a high pressure gas stream in, for example, a power recovery turbine rather than to release the gas through an expansion valve. Useful power can be provided for minimal operating cost and there is a significant environmental benefit.

It should be understood that there is a practical limit to the complexity of highly integrated systems which can be effectively operated. Difficulties can occur during for example, sequential start up and during major upsets. Thus the absolute maximum of process integration may not always produce the best environmental performance in practice.

Indicative BAT requirements for further energy-efficiency requirements (Sheet 1 of 2) Climate Change Agreement or Trading Agreement.

1 The following techniques should be implemented where they are judged to be BAT based on a cost/ benefit appraisal according to the methodology provided in Appendix 4 of the guidance note H2 Energy efficiency for IPPC.

Energy-efficiency techniques

Energy supply techniques

- 2 The following techniques should be considered:
 - use of Combined Heat and Power (CHP)
 - · generation of energy from waste
 - use of less polluting fuels
- 3 The Operator should provide justification that the proposed or current situation represents BAT, irrespective of whether a CCA or Trading Agreement is in place, where there are other BAT considerations involved, such as:
 - the choice of fuel impacts upon emissions other than carbon, for example, sulphur in fuel
 - where the potential minimisation of waste emissions by recovery of energy from waste conflicts with energy efficiency requirements

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Indicative BAT requirements for further energy-efficiency requirements (Sheet 2 of 2) Climate Change Agreement or Trading Agreement.

Where there is an on-site combustion plant other guidance is also relevant. For plants greater than 50MW, Operators should consult the IPC guidance on power generation (reference IPC S2 1.01 Combustion Processes: Large boilers and furnaces 50MW(th) and over and supplement IPC S3 1.01 Combustion Processes). Operators of plant of 20-50MW should consult the Local Authority Air Pollution Control guidance. On IPPC installations this guidance will be generally applicable to plant under 20MW also. For incineration plant S2.5.01 Waste Incineration should be consulted (available from the EA website).

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2.8 Accidents

This section covers accidents and their consequences. It is not limited to major accidents but includes spills and abnormal operation.

Some installations will also be subject to the Control of Major Accident Hazards Regulations 1999 (COMAH) (see Appendix 2 for equivalent legislation in Scotland and Northern Ireland). IPPC and COMAH sometimes overlap and some systems and information for both regimes may be interchangeable.

The COMAH regime applies to major hazards. For accidents covered by COMAH, refer to any reports already held by the Regulator. However, the accident provisions under IPPC may fall beneath the threshold for major accident classification under COMAH, so Operators also need to consider smaller accidents and abnormal operation as well. Guidance (see the COMAH guides), prepared in support of the COMAH Regulations may also help IPPC Operators (whether or not they are covered by the COMAH regime), in considering ways to reduce the risks and consequences of accidents.

General management requirements are covered in Section 2.1. For accident management, there are three particular components:

- identification of the hazards posed by the installation/activity
- assessment of the risks (hazard x probability) of accidents and their possible consequences
- implementation of measures to reduce the risks of accidents, and contingency plans for any accidents that do occur

Indicative BAT requirements for accidents and abnormal operations (Sheet 1 of 3) Describe the documented system that you propose to be used to identify, assess and minimise the environmental risks and consequence of accidents.

- 1 A structured accident management plan should be submitted to the Regulator that should:
- 2 Identify the hazards to the environment posed by the installation. Particular areas to consider may include, but should not be limited to, the following:
 - · transfer of substances (for example, loading or unloading from or to vessels)
 - overfilling of vessels
 - · failure of plant and/or equipment (for example, over-pressure of vessels and pipework, blocked drains)
 - failure of containment (such as bund and/or overfilling of drainage sumps)
 - failure to contain firewaters
 - making the wrong connections in drains or other systems
 - · preventing incompatible substances coming into contact
 - unwanted reactions and/or runaway reactions
 - emission of an effluent before adequate checking of its composition has taken place ٠
 - · steam main issues
 - vandalism
- 3 assess the risks. Having identified the hazards, the process of assessing the risks should address six basic questions:
 - how likely are they to occur? (source frequency)
 - what gets out and how much? (risk evaluation of the event)
 - where does it end up? (predictions for the emission what are the pathways and receptors?)
 - what are the consequences? (consequence assessment the effects on the receptors)

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Indicative BAT requirements for accidents and abnormal operations (Sheet 2 of 3) Describe the documented system that you propose to be used to identify, assess and minimise the environmental risks and consequence of accidents.

- what are the overall risks? (determination of the overall risk and its significance to the environment)
- what can prevent or reduce the risk? (risk management measures to prevent accidents and/or reduce their environmental consequences)
- 4 The depth and type of assessment will depend on the characteristics of the installation and its location. The main factors to take into account are:
 - the scale and nature of the accident hazard presented by the installation and the activities
 - the risks to areas of population and the environment (receptors)
 - the nature of the installation and complexity of the activities and the relative difficulty in deciding and justifying the adequacy of the risk-control techniques
- 5 **identify the techniques necessary to reduce the risks.** The following techniques are relevant to most installations:
 - an inventory should be maintained of substances, present or likely to be present, which could have environmental consequences if they escape. Do not forget that many apparently innocuous substances can be environmentally damaging if they escape (for example, a tanker of milk spilled into a watercourse could destroy its ecosystem). The Permit will require the Regulator to be notified of any changes to the inventory
 - procedures should be in place for checking raw materials and wastes to ensure compatibility with other substances with which they may accidentally come into contact
 - · adequate storage arrangements for raw materials, products and wastes should be provided
 - to ensure that control is maintained in emergency situations, consideration should be given to process design alarms, trips and other control aspects, for example, automatic systems based on microprocessor control and passing valve control, tank level readings such as ultrasonic gauges, high-level warnings and process interlocks and process parameters
 - preventative techniques, such as suitable barriers to prevent damage to equipment from the movement of vehicles, should be included as appropriate
 - appropriate containment should be provided, for example, bunds and catchpots, building containment
 - techniques and procedures should be implemented to prevent overfilling of storage tanks (liquid or powder), for example, level measurement, independent high-level alarms, highlevel cut-off, and batch metering
 - where the installation is situated in a floodplain, consideration should be given to techniques which will minimise the risk that flooding may either cause a pollution incident or make one worse
 - installation security systems to prevent unauthorised access should be provided as appropriate and should include maintenance arrangements where necessary
 - there should be an installation log/diary to record all incidents, near-misses, changes to procedures, abnormal events and findings of maintenance inspections
 - · procedures should be established to identify, respond to and learn from such incidents
 - · roles and responsibilities of personnel involved in accident management identified
 - clear guidance should be available on how each accident scenario should be managed, for example, containment or dispersion, to extinguish fires or let them burn
 - procedures should be in place to avoid incidents occurring as a result of poor communication among operations staff during shift changes and maintenance or other engineering work
 - · safe shutdown procedures should be in place

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Indicative BAT requirements for accidents and abnormal operations (Sheet 3 of 3) Describe the documented system that you propose to be used to identify, assess and minimise the environmental risks and consequence of accidents.

- communication routes should be established with relevant authorities and emergency services both before and in the event of an accident. Post-accident procedures should include the assessment of harm caused and steps needed to redress this
- appropriate control techniques should be in place to limit the consequences of an accident, such as oil spillage equipment, isolation of drains, alerting of relevant authorities and evacuation procedures
- · personnel training requirements should be identified and provided
- the systems for the prevention of fugitive emissions are generally relevant (Section 2.2.4 and Section 2.2.5) and in addition, for drainage systems:
 - procedures should be in place to ensure that the composition of the contents of a bund sump, or sump connected to a drainage system, are checked before treatment or disposal
 - drainage sumps should be equipped with a high-level alarm or sensor with automatic pump to storage (not to discharge)
 - there should be a system in place to ensure that sump levels are kept to a minimum at all times
 - high-level alarms and the like should not be routinely used as the primary method of level control
- adequate redundancy or standby plant should be provided with maintenance and testing to the same standards as the main plant
- process waters, site drainage waters, emergency firewater, chemically contaminated waters and spillages of chemicals should, where appropriate, be contained and, where necessary, routed to the effluent system, with provision to contain surges and storm-water flows, and treated before emission to controlled waters or sewer. Sufficient storage should be provided to ensure that this could be achieved. There should also be spill contingency procedures to minimise the risk of accidental emission of raw materials, products and waste materials and to prevent their entry into water. Any emergency firewater collection system should also take account of the additional firewater flows or fire-fighting foams. Emergency storage lagoons may be needed to prevent contaminated firewater reaching controlled waters (see the Releases to water references)
- consideration should be given to the possibility of containment or abatement for accidental emissions from vents and safety relief valves/bursting discs. Where this may be inadvisable on safety grounds, attention should be focused on reducing the probability of the emission

Emissions

controls

Energy

Monitoring

Closure

2.9 Noise

Noise is a constant feature of most LVOC processes, and there are some features specific to the sector.

Accidents

The use of large machines such as compressors and pumps which are sometimes installed without enclosure can give rise to high noise levels. Rotary rather than reciprocating machines generally produce less vibration and pulsation and are widely installed for all except specialised very high pressure applications. Low noise designs should be chosen where available and installed preferably in an enclosure.

Particularly noisy machines such as compactors and pelletisers should be installed in a noise control booth or the source of noise should be encapsulated.

Combustion equipment such as furnaces and heaters can produce a low resonant sound detectable at a considerable distance. This can be moderated by good design. Flares are a particular source of noise, often associated with steam injection for smoke suppression. The use of flares should be limited to emergency conditions. Good design of flares tips can lessen the need for high rates of steam injection and provide quieter operation.

The operation of safety valves and other release devices for high pressure systems can be extremely noisy. Where possible without compromising safety, suitable silencers should be fitted. The blow-off from boilers and air compressors, for example during start up, should be minimised and silencers should be provided.

Careful design of building layout and consideration of the proximity of potential receptors such as residential areas can sometimes avoid problems in operation.

Within this section "noise" should be taken to refer to "noise and/or vibration" as appropriate, detectable beyond the site boundary.

Where noise issues are likely to be relevant, the Operator will be required, in the Application, to provide information on the following: (for more details see H3 Part 1 Noise)

- the main sources of noise and vibration that will fall within the IPPC installation and also on Infrequent sources of noise and vibration
- the nearest noise-sensitive sites
- · conditions/limits imposed under other regimes
- the local noise environment
- any environmental noise measurement surveys, modelling or any other noise measurements
- any specific local issues and proposals for improvements.

The level of detail supplied should be in keeping with the risk of causing noise-related annoyance at sensitive receptors.

Where an installation poses no risk of noise-related environmental impact because the activities undertaken are inherently quiet, this should be justified and no further information relating to noise need normally be supplied. It should, however, be remembered that there can still be an underlying level of annoyance without complaints being made.

The PPC Regulations require installations to be operated in such a way that "all the appropriate preventative measures are taken against pollution, in particular through the application of BAT". The definition of pollution includes "emissions that may be harmful to human health or the quality of the environment, cause offence to human senses or impair or interfere with amenities and other legitimate uses of the environment". BAT is therefore likely to be similar, in practice, to the requirements of the statutory nuisance legislation, which requires the use of "best practicable means" to prevent or

Introduction			Techniques for pollution control			Emissions			Impact		
In-process Emissions Management controls		Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

minimise noise nuisance. It is understood that raw material handling can generate noise where glass is being recycled or broken up. It is suggested that consideration be given to the use of sonic booths or sound proofing to control the generation of noise where such activities are being carried out.

In the case of noise, "offence to any human senses" can normally be judged by the likelihood of complaints, but in some cases it may be possible to reduce noise emissions still further at reasonable costs, and this may exceptionally therefore be BAT for noise emissions.

For advice on how noise and/or vibration related limits and conditions will be determined see H3 Part 1 Noise

Indicative BAT requirements for noise and vibration

Describe the main sources of noise and vibration (including infrequent sources); the nearest noisesensitive locations and relevant environmental surveys which have been undertaken; and the proposed techniques and measures for the control of noise.

- 1 The Operator should employ basic good practice measures for the control of noise, including adequate maintenance of any parts of plant or equipment whose deterioration may give rise to increases in noise (for example, maintenance of bearings, air handling plant, the building fabric as well as specific noise attenuation measures associated with plant, equipment or machinery).
- 2 The Operator should also employ such other noise control techniques to ensure that the noise from the installation does not give rise to reasonable cause for annoyance, in the view of the Regulator and, in particular, should justify where either Rating Levels (LAeq,T) from the installation exceed the numerical value of the Background Sound Level (LA90,T).
- 3 Further justification will be required should the resulting field rating level (LAR,TR) exceed 50 DB by day and a facade rating level exceed 45 DB by night, with day being defined as 07:00 to 23:00 and night 23:00 to 07:00.
- 4 In some circumstances "creeping background" may be an issue. Where this has been identified in pre application discussions or in previous discussions with the local authority, the Operator should employ such noise control techniques as are considered appropriate to minimise problems to an acceptable level within the BAT criteria.
- 5 Noise surveys, measurement, investigation (which can involve detailed assessment of sound power levels for individual items of plant) or modelling may be necessary for either new or existing installations depending upon the potential for noise problems. Operators may have a noise management plan as part of their management system.

Introduction			Techniques for pollution control			Emissions			Impact		
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

2.10 Monitoring

This section describes monitoring and reporting requirements for emissions to all environmental media. Guidance is provided for selecting the appropriate monitoring methodologies, frequency of monitoring, compliance-assessment criteria and environmental monitoring.

2.10.1 Emissions monitoring

Indicative BAT requirements for emissions monitoring (Sheet 1 of 2) Describe the proposed measures for monitoring emissions, and the frequency, measurement methodology and evaluation procedure proposed.

- 1 The following monitoring parameters and frequency are normally appropriate in this sector. Generally, monitoring should be undertaken during commissioning, start-up, normal operation and shut-down unless the Regulator agrees that it would be inappropriate to do so.
- 2 Continuous monitoring (or at least sampling in the case of water) and recording are likely to be required under the following circumstances:
 - Where the potential environmental impact is significant or the concentration of substance varies widely.
 - Where a substance is abated continuous monitoring of the substance is required to show the performance of the abatement plant. For example continuous monitoring of dust is needed after a fabric filter to show the effectiveness of the filter and indicate when maintenance is needed, or sampling BOD from an effluent treatment plant.
 - Where other control measures are required to achieve satisfactory levels of emission (e.g. material selection).
- 3 Where effective surrogates are available, they may be used to minimise monitoring costs.
- 4 Where monitoring shows that substances are not emitted in significant quantities, it may be possible to reduce monitoring frequency.
- 5 For analysis techniques and compliance criteria see **Appendix 1**.

Monitoring and reporting of emissions to air

- 6 Where appropriate, periodic visual and olfactory assessment of releases should be undertaken to ensure that all final releases to air should be essentially colourless, free from persistent trailing mist or fume and free from droplets.
- 7 The Operator should also have a fuller analysis carried out covering a broad spectrum of substances to establish that all relevant substances have been taken into account when setting the release limits. This should cover the substances listed in Schedule 5 of the Regulations unless it is agreed with the Regulator that they are not applicable. The need to repeat such a test will depend upon the potential variability in the process and, for example, the potential for contamination of raw materials. Where there is such potential, tests may be appropriate.

Int	Introduction			Techniques for pollution control			Emissions			Impact		
		Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

Indicative BAT requirements for emissions monitoring (Sheet 2 of 2) Describe the proposed measures for monitoring emissions, and the frequency, measurement methodology and evaluation procedure proposed.

- 8 Any substances found to be of concern, or any other individual substances to which the local environment may be susceptible and upon which the operations may impact, should also be monitored more regularly. This would particularly apply to the common pesticides and heavy metals. Using composite samples is the technique most likely to be appropriate where the concentration does not vary excessively.
- In some sectors there may be releases of substances that are more difficult to measure and whose capacity for harm is uncertain, particularly when combined with other substances.
 "Whole effluent toxicity" monitoring techniques can therefore be appropriate to provide direct measurements of harm, for example, direct toxicity assessment. See Section 2.2.2.

Monitoring and reporting of waste emissions

- 10 For waste emissions, the following should be monitored and recorded:
 - the physical and chemical composition of the waste
 - · its hazard characteristics
 - · handling precautions and substances with which it cannot be mixed

Table 2.3: Monitoring of process elements released to controlled waters should include at least:

Parameter	Monitoring frequency
Flow rate	Continuous and integrated daily flow rate
рН	Continuous
Temperature	Continuous
COD/BOD	Flow weighted sample or composite samples, weekly analysis, reported as flow weighted monthly averages
Turbidity	Continuous
Oil	Daily or weekly analysis (depending on risk or history)

Introduction			Techniques for pollution control			Emissions			Impact		
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2.10.2 Environmental monitoring (beyond installation)

Indicative BAT requirements for environmental monitoring (beyond installation) Describe the proposed measures for any environmental monitoring, and the frequency, measurement methodology and evaluation procedure proposed.

- 1 The Operator should consider the need for environmental monitoring to assess the effects of emissions to controlled water, groundwater, air or land, or emissions of noise or odour.
- 2 Environmental monitoring may be required, for example, when:
 - · there are vulnerable receptors
 - the emissions are a significant contributor to an Environmental Quality Standard (EQS) that may be at risk
 - · the Operator is looking for departures from standards based on lack of effect on the environment;
 - · to validate modelling work.
- 3 The need should be considered for:
 - · groundwater, where it should be designed to characterise both quality and flow and take into account short- and long-term variations in both. Monitoring will need to take place both upgradient and down-gradient of the site
 - surface water, where consideration will be needed for sampling, analysis and reporting for upstream and downstream quality of the controlled water
 - · air, including odour
 - · land contamination, including vegetation, and agricultural products
 - · assessment of health impacts
 - noise

- Where environmental monitoring is needed, the following should be considered in drawing up 4 proposals:
 - · determinands to be monitored, standard reference methods, sampling protocols
 - monitoring strategy, selection of monitoring points, optimisation of monitoring approach
 - · determination of background levels contributed by other sources
 - · uncertainty for the employed methodologies and the resultant overall uncertainty of measurement
 - quality assurance (QA) and quality control (QC) protocols, equipment calibration and maintenance, sample storage and chain of custody/audit trail
 - · reporting procedures, data storage, interpretation and review of results, reporting format for the provision of information for the Regulation
- 5 Guidance on air quality monitoring strategies and methodologies can be found in Monitoring Guidance.

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In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

2.10.3 Monitoring of process variables

Indicative BAT requirements for monitoring of process variables Describe the proposed measures for monitoring those process variables that may have a significant effect on emissions.

- 1 Some process variables may affect the environment and these should be identified and monitored as appropriate. Examples might be:
 - raw materials monitoring for contaminants where contaminants are likely and there is inadequate supplier information (see Section 2.4.1)
 - · plant efficiency where it has an environmental relevance
 - abatement equipment performance (e.g. bag filter pressure drop)
 - energy consumption across the plant and at individual points-of-use in accordance with the energy plan. Frequency – normally continuous and recorded
 - fresh water use across the activities and at individual points-of-use should be monitored as part of the water-efficiency plan (see Section 2.4.3). Frequency – continuous and recorded

2.10.4 Monitoring standards (Standard Reference Methods)

The Environment Agency has introduced its Monitoring Certification Scheme (MCERTS) to improve the quality of monitoring data and to ensure that the instrumentation and methodologies employed for monitoring are fit for purpose. Performance standards have been published for continuous emissions monitoring systems (CEMs), ambient air quality monitoring systems (CAMs), chemical testing of soils and manual stack emissions monitoring. Other MCERTS standards are under development to cover portable emissions monitoring equipment, water monitoring instrumentation, data acquisition and Operators' own arrangements, such as installation, calibration and maintenance of monitoring equipment, position of sampling ports and provision of safe access for manual stack monitoring.

The following should be described in the application, indicating which monitoring provisions comply with MCERTS requirements or where other arrangements have been made:

- monitoring methods and procedures (selection of Standard Reference Methods)
- justification for continuous monitoring or spot sampling
- · reference conditions and averaging periods
- · measurement uncertainty of the proposed methods and the resultant overall uncertainty
- criteria for the assessment of non-compliance with Permit limits and details of monitoring strategy aimed at demonstration of compliance
- reporting procedures and data storage of monitoring results, record keeping and reporting intervals for the provision of information to the Regulator
- procedures for monitoring during start-up and shut-down and abnormal process conditions
- drift correction calibration intervals and methods
- the accreditation held by samplers and laboratories or details of the people used and the training/ competencies

Introduction			Techniques for pollution control			Emissions			Impact		
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Indicative BAT requirements for monitoring standards (Standard Reference Methods) Describe the methods proposed for analysing emissions and for environmental monitoring

1 As far as possible, Operators should ensure their monitoring arrangements comply with the requirements of MCERTS where available, for example using certified instruments and equipment, and using a stack testing organisation accredited to MCERTS standards. Where the monitoring arrangements are not in accordance with MCERTS requirements, the Operator should provide justification and describe the monitoring provisions in detail. See MCERTS approved equipment link via http://www.environment-agency.gov.uk/business/mcerts for future information on MCERTS and a listing of MCERTS equipment.

Sampling and analysis standards

- 2 The analytical methods given in **Appendix 1** should be used. In the event of other substances needing to be monitored, standards should be used in the following order of priority:
 - Comité Européen de Normalisation (CEN)
 - British Standards Institution (BSI)
 - International Standardisation Organisation (ISO)
 - United States Environmental Protection Agency (US EPA)
 - American Society for Testing and Materials (ASTM)
 - Deutches Institut f
 ür Normung (DIN)
 - Verein Deustcher Ingenieure (VDI)
 - Association Française de Normalisation (AFNOR)
- 3 Further guidance on standards for monitoring gaseous releases relevant to IPC/IPPC is given in the Monitoring Guidance. A series of updated Guidance Notes covering this subject is being prepared. This guidance specifies manual methods of sampling and analysis that will also be suitable for calibration of continuous emission monitoring instruments. Further guidance relevant to water and waste is available from the publications of the Standing Committee of Analysts.
- 4 If in doubt the Operator should consult the Regulator.

Raw materials

Techniques for pollution control Waste Waste handling recovery of disposal

Emissions

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2.11 Closure

The PPC Regulations require an Applicant to submit a site report, describing the condition of the site, as part of the application. Guidance on this is in Annex C of the Guide for Applicants (see Closure) or Guidance for SEPA Staff On Land and Groundwater Considerations for PPC Part A Installations (Scotland) (see PPC Part A Installations: Guide for Applicants (Scotland)).

Accidents

Indicative BAT requirements for closure (Sheet 1 of 2)

Describe the proposed measures, upon definitive cessation of activities, to avoid any pollution risk and to return the site of operation to a satisfactory state (including measures relating to the design and construction of the installation, where appropriate).

1 **Operations during the IPPC Permit**

Operations during the life of the IPPC Permit should not lead to any deterioration of the site if the requirements of the other sections of this and the specific-sector notes are adhered to. Should any instances arise which have, or might have, impacted on the state of the site, the Operator should record them along with any further investigation or ameliorating work carried out. This will ensure that there is a coherent record of the state of the site throughout the period of the IPPC Permit. This is as important for the protection of the Operator as it is for the protection of the environment. Any changes to this record should be submitted to the Regulator.

Steps to be taken at the design-and-build stage of the activities 2

Care should be taken at the design stage to minimise risks during decommissioning. For existing installations, where potential problems are identified, a programme of improvements should be put in place to a timescale agreed with the Regulator. Designs should ensure that:

- underground tanks and pipework are avoided where possible (unless protected by secondary containment or a suitable monitoring programme)
- there is provision for the draining and clean-out of vessels and pipework prior to dismantling
- · lagoons and landfills are designed with a view to their eventual clean-up or surrender
- · insulation is provided that is readily dismantled without dust or hazard
- · materials used are recyclable (having regard for operational or other environmental objectives)

3 The site-closure plan

A site closure plan should be maintained to demonstrate that, in its current state, the installation can be decommissioned to avoid any pollution risk and return the site of operation to a satisfactory state. The plan should be kept updated as material changes occur. Common sense should be used in the level of detail, since the circumstances at closure will affect the final plans. However, even at an early stage, the closure plan should include:

- either the removal or the flushing out of pipelines and vessels where appropriate and their complete emptying of any potentially harmful contents
- · plans of all underground pipes and vessels
- · the method and resource necessary for the clearing of lagoons
- the method of ensuring that any on-site landfills can meet the equivalent of surrender conditions
- · the removal of asbestos or other potentially harmful materials unless agreed that it is reasonable to leave such liabilities to future owners
- methods of dismantling buildings and other structures, see Ref 1 which gives guidance on the protection of surface and groundwater at construction and demolition-sites

Introduction			Techniques for pollution control			Emissions			Impact		
In-process controls	Emissions controls	Management	Raw materials	Waste handling	Waste recovery or disposal	Energy	Accidents	Noise	Monitoring	Closure	Installation issues

Indicative BAT requirements for closure (Sheet 2 of 2)

Describe the proposed measures, upon definitive cessation of activities, to avoid any pollution risk and to return the site of operation to a satisfactory state (including measures relating to the design and construction of the installation, where appropriate).

- testing of the soil to ascertain the degree of any pollution caused by the activities and the need for any remediation to return the site to a satisfactory state as defined by the initial site report
- 4 For existing activities, the Operator should complete any detailed studies, and submit the siteclosure plan as an improvement condition to a timescale to be agreed with the Regulator but in any case within the timescale given in Section 1.1 (Note that radioactive sources are not covered by this legislation, but decommissioning plans should be co-ordinated with responsibilities under the Radioactive Substances Act 1993.)

In-process controls Emissions

controls

Energy

Impact Monitoring

Closure Issues for multi-operato

Installations

2.12 Issues for multi-operator Installations

In some cases it is possible that actions that benefit the environmental performance of the overall installation will increase the emissions from one Permit-holder's activities. For example, taking treated effluent as a raw water supply will probably slightly increase emissions from that activity, but could dramatically cut the total emissions from the whole installation.

Where you are not the only Operator of the installation, describe the proposed techniques and measures (including those to be taken jointly by yourself and other Operators) for ensuring the satisfactory operation of the whole installation

Indicative BAT requirements for installation wide issues

If you are not the only Operator of the installation, describe the proposed techniques and measures taken by you and the other Operators to ensure satisfactory environmental performance of the installation as a whole.

- 1 The Operator should consider possibilities for minimising environmental impact to the environment as a whole, by operating together with other Permit holders. Possibilities include:
 - Communication procedures between the various Permit-holders; in particular those needed to ensure that the risk of environmental incidents is minimised.
 - Benefiting from the economies of scale to justify the installation of a CHP plant.
 - The combining of combustible wastes to justify a combined waste-to-energy/CHP plant.
 - The waste from one activity being a possible feedstock for another.
 - The treated effluent from one activity being of adequate quality to be the raw water feed for another activity.
 - The combining of effluent to justify a combined or upgraded effluent-treatment plant.
 - The avoidance of accidents from one activity that may have a detrimental knock-on effect on the neighbouring activity.
 - Land contamination from one activity affecting another or the possibility that one Operator owns the land on which the other is situated.

Emissions inventory

Emissions

benchmarks

3 Emission benchmarks

3.1 Emissions inventory

The Regulations require the Applicant to describe the nature, quantities and sources of foreseeable emissions into each medium. This will be done by completing the inventory of emission and consumption in the H1 software tool. The information required is as follows.

Provide a table of significant emissions of substances (except noise, vibration, odour and heat which are covered in their respective sections) that will result from the proposals and should include, preferably in order of significance:

- substance (where the substance is a mixture, for example, VOCs or COD, separate identification of the main constituents or inclusion of an improvement proposal to identify them)
- · source, including height, location and efflux velocity
- media to which it is released
- any relevant EQS or other obligations
- benchmark

Techniques

- proposed emissions normal/max expressed, as appropriate for:
 - mass/unit time
 - concentration
 - annual mass emissions
- statistical basis (average, percentile etc.)
- · notes covering the Operators confidence in his ability to meet the benchmark values
- · if intermittent, the appropriate frequencies
- · plant loads at which the data is applicable
- whether measured or calculated (the method of calculation should be provided)

The response should clearly state whether the emissions are current emission rates or those planned following improvements, and should cover emissions under both normal and abnormal conditions for:

- point-source emissions to surface water, groundwater and sewer
- waste emissions
- point-source emissions to air
- significant fugitive emissions to all media, identifying the proportion of each substance released that is due to fugitives rather than point-source releases
- abnormal emissions from emergency relief vents, flares and the like
- · indirect and direct emission of carbon dioxide associated with energy consumed or generated

Emissions of carbon dioxide associated with energy use should be broken down by energy type and, in the case of electricity, by source, for example, public supply, direct supply or on-site generation. Where energy is generated on-site, or from a direct (non-public) supplier, the Operator should specify and use the appropriate factor. Standard factors for carbon dioxide emissions are provided in the guidance note H2 Energy efficiency for IPPC.

Where VOCs are released, the main chemical constituents of the emissions should be identified.

Emissions Emissions inventory

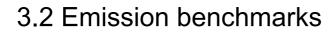
benchmarks

For waste, emissions relate to any wastes removed from the installation, or disposed of at the installation under the conditions of the Permit, for example, landfill. Each waste should have its composition determined and the amounts expressed in terms of cubic metres or tonnes per month. A suitable table on which to record this information is provided in the electronic version of this Guidance Note.

Indicative BAT requirements for emission benchmarks

Describe the nature, quantities and sources of foreseeable emissions into each medium (which will result from the techniques proposed in Section 2).

- The Operator should compare the emissions with the benchmark values given in the remainder 1 of this Section.
- 2 Where the benchmarks are not met, the Operator should revisit the responses made in Section 2 as appropriate and make proposals for improvements or justify not doing so as part of the BAT assessment.



Introduction to emission benchmarks

Guidance is given below on release concentrations or mass release rates achievable for key substances using the best combination of techniques. These BAT-based benchmarks are not mandatory release limits and reference should be made to Section 1 and the Guide for Applicants regarding their use.

3.2.1 Emissions to air associated with the use of BAT

The emissions quoted below are daily averages based upon continuous monitoring during the period of operation. See Section 3.2.6 for the standard conditions that should be applied. Care should always be taken to convert benchmark and proposed releases to the same reference conditions for comparison. To convert measured values to reference conditions, see the Monitoring Guidance for more information. The benchmarks given do not take sampling, analytical errors, or uncertainties into account. These will be considered when setting an ELV for a Permit.

Limits in Permits may be set for mean or median values over long or short periods. The periods and limits selected should reflect:

- the manner in which the emission may impact upon the environment
- likely variations which will arise during operation within BAT
- possible failure modes and their consequences
- the capabilities of the monitoring and testing system employed

Where emissions are expressed in terms of concentrations and where continuous monitors are employed, it is recommended that limits are defined such that:

- not more than one calendar monthly average during any rolling twelve month period shall exceed the benchmark value by more than 10%
- not more than one half hour period during any rolling 24 hour period shall exceed the benchmark value by more than 50% (for the purpose of this limit half hourly periods commence on the hour and the half hour)

Where spot tests are employed:

- the half hour limit above shall be applied over the period of the test
- the mean of three consecutive tests taken during a calendar year shall not exceed the benchmark value by more than 10%

The pollutants which will be specifically monitored, and particularly those that will have emission limit values (ELVs) set, should be selected according to their potential for emission and environmental impact. They will be installation-specific so, where relevant, the process descriptions in Section 2.2, should be consulted. An indication of relevant iactivities, other than those for the manufacture of the substance, is given in the "source" column in Table 3.1 below.

Emissions Inventory

Emission benchmarks

Further details for certain illustrative processes can be found in the LVOC BREF Notes:

Table 3.1: Relevant Processes

Determinand	Source processes	Benchmark value mg/m ³	Type and fre- quency of monitoring	Comments; Abatement sys- tem
Acrylamide		5	Continuous	
Acrylonitrile	Adiponitrile, acryla- mide, ABS polymers	0.5 - 2	Continuous	0.5 mg/m ³ for Incineration, 2 for scrubbing
Amines (total as DMA)	DMAE, DMCHA, DMF, DMAC	10	Continuous	
Ammonia	Amines, eth- anolamines	10	Continuous	
Benzene	Ethylbenzene, nitrobenzene, cumene etc.	5	Continuous	
Bromine	Brominated hydro- carbons	10	Continuous	
Butadiene	Hydrocarbons	5	Continuous	
Cadmium and cpds. (as Cd)(a)	Incineration	0.1	Periodic See HWID	
Carbon disulphide	Dithiocarbamates, thiophene, mercap- tobenzothiazole	5	Continuous	
Carbon monoxide	Combustion, incin- eration, acetic acid, OXO processes, DMF	100	Continuous	
Chlorine	Chlorinated hydro- carbons	10	Continuous	
1,2-dichloroethane	VCM	1 - 5	Continuous	1 mg/m ³ for incin- eration
Ethylene oxide	Ethylene glycol, gly- colethers, eth- anolamines, polyglycols, choline chloride, hydroxy acrylates etc.	2	Continuous	Water scrubbing
Formaldehyde	Resins	2	Continuous	
Hydrogen bromide	Brominated hydro- carbons	5	Continuous	
Hydrogen chloride	Chlorinated hydro- carbons	10	Continuous	
Hydrogen cyanide	Acrylonitrile	2	Continuous	
Hydrogen fluoride	Hydrofluorocar- bons, alkylation processes	5	Continuous	
Hydrogen iodide		5	Periodic (Monthly)	
Hydrogen sulphide	Dithiocarbamates, thiols, thiophene	5	Continuous	

Emissions Inventory Emission benchmarks

Table 3.1: Relevant Processes

Determinand	Source processes	Benchmark	Type and fre-	Comments:
Determinant	Source processes	value mg/m ³	quency of monitoring	Abatement sys- tem
Heavy metals (excl. Hg, Cd) (a)	Incineration, cata- lyst regeneration	1.5	Periodic See HWID	
lodine	Acetic acid	10	Periodic (Monthly)	
Maleic anhydride	Resins	5	Periodic (Monthly)	
Mercury and cpds. (as Hg) (a)	Incineration	0.05	Periodic See HWID	
Methyl mercaptan		2	Continuous	
Nitrobenzene	Aniline	5	Continuous	
Organic sulphides and mercaptans (as H2S)		2	Continuous	
Oxides of nitrogen (total acid forming as NO2)	Nitration, combus- tion	50 - 200	Continuous	50 mg/m ³ for SCR; 200 for wet scrubbing
Oxides of sulphur (as SO2)	Sulphonation, com- bustion	50 - 100	Continuous	50 mg/m ³ for wet scrubbing; 100 for semi-dry
Particulate matter	Polymers, Resins	5 - 20	Continuous	5 mg/m ³ for fab- ric filters; 20 for ESP
Phenols, cresols and xylols (as phenol)	Cumene, adipic acid, resins	10	Continuous/ Periodic (Monthly)	
Trimethylamine		2	Continuous	
Vinyl chloride (b)	PVC, copolymers See Note b	1 - 5	Continuous	1 mg/m ³ for incin- eration
VOC total Class A (c)	See Note c	20	Continuous	
VOC Total Class B (c) (as carbon)	See Note c	75	Continuous	
Dioxins and furans (ng TEQ /m ³)	Incinerators, DCE and VCM processes	0.1	Periodic	See HWID

Note (a):

- The reference conditions applicable to these levels are: temperature 273 K (0oC), pressure 101.3 kPa (1 atmosphere), 3% oxygen, no correction for water vapour.
- Where the term "expressed as" is used, a correction should be carried out using the ratio of the atomic or molecular weights of the substances as appropriate.
- All releases should be essentially colourless, free from persistent trailing mist or fume, and free from droplets.
- Releases from the processes should not give rise to an offensive odour noticeable outside the site where the process is carried on.

Emission Emissions Inventory

benchmarks

Note (b):

- OSPARCOM Recommendation 98/4 relates to BAT for the manufacture of vinyl chloride monomer, 98/5 to suspension PVC.
- For PVC manufacture, the following release rates are achievable:
 - Emulsion process total VCM release from all vessel vents1.0 kg/tonne PVC
 - Suspension process total VCM release from all vents 0.1 kg/tonne PVC

Note (c):

- Releases of VOCs should be individually identified, where possible. The VOC concentration levels apply where the following total mass release rates are exceeded:
 - Total Class A 100g/h (expressed as individual VOCs)
 - Total Class B 5 tonnes/yr or 2 kg/h, whichever is the lower (expressed as carbon)
- Note however that releases below these mass emission rates may not be trivial, and so may still require controls and the setting of appropriate release limits.
- The use of a release concentration limit is not normally appropriate in the case of a release from an air-deficient saturated vapour space such as a storage tank or process vessel. An approach based on limiting total mass released or mass per unit of production is likely to be more effective.
- The term "volatile organic compounds" includes all organic compounds released to air in the gas phase. See also Appendix 3.

3.2.2 Emissions to water associated with the use of BAT

Wastewater treatment systems can maximise the removal of metals using precipitation, sedimentation and possibly filtration. The reagents used for precipitation may be hydroxide, sulphide or a combination of both, depending on the mix of metals present. It is also practicable in many cases to re-use treated water.

Where automatic sampling systems are employed, limits may be defined such that:

not more than 5% of samples shall exceed the benchmark value

Where spot samples are taken:

no spot sample shall exceed the benchmark value by more than 50%

The determinands should be selected according to the potential for their emission from the process being considered. Refer to the process descriptions in Section 2.2.

Further detail for certain illustrative processes can be found in the LVOC BREF notes:

Table 3.2: Emissions to water

Substance	Level (mg/l) Note (a)
Total hydrocarbon oil content (IR method)	1-3
Biological oxygen demand (BOD) (5 day ATU @ 20oC)	20-30
Chemical oxygen demand (COD) (2 hour)	30-125
Total nitrogen (as N)	10-15
Suspended solids (dried @ 105oC)	20-30

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Table 3.2: Emissions to water

Substance	Level (mg/l) Note (a)
Halogenated Organic Compounds AOX Notes (b) and (d)	1
Mercury	0.05
Cadmium	0.2
Copper, chromium, nickel and lead (each)	0.5
Zinc and tin (each)	2

Note (a)

The levels given here are ranges achievable after effluent treatment and are not release limits. They are given on the basis of flow weighted monthly averages.

For pollutants resistant to biodegradation, achievement of the levels will require isolation at source and separate specialised treatment.

On-site effluent treatment is preferred for these processes. Where discharge to sewer is proposed, the applicant should demonstrate that this option represents BAT, taking into account:

·the substances released and their separability and degradability

the type of sewage treatment available

the security of the sewage treatment system, eg with regard to storm overflow; and

the relative performance of the available sewage treatment compared with that of the site dedicated option

Compliance with limits imposed by the sewage undertaker does not guarantee compliance with BAT.

Note (b)

EC Directive 90/415/EEC gives limits for releases to water from the production and use of 1,2dichloroethane, trichloroethylene, perchloroethylene and trichlorobenzene.

Note (c)

OSPARCOM Recommendation 98/4 includes values for discharges to water from the manufacture of VCM. OSPARCOM Recommendation 98/5 and / include values for discharges to water from the manufacture of suspension PVC and emulsion PVC respectively.

Note (d)

SI 1989 No 2286 and SI 1998 No 389 give annual mean concentration standards for certain dangerous substances in receiving waters.

3.2.3 Standards and obligations

In addition to meeting the requirements of BAT, there are other national and international standards and obligations that must either be safeguarded through the IPPC Permit or, at least, taken into account in setting Permit conditions. This is particularly the case for any EC based EQSs.

Emissions Inventory Emission benchmarks

EC-based EQ standards

IPPC: A Practical Guide explains how these should be taken into account and contains an annex listing the relevant standards. (See **Appendix 2** for equivalent legislation in Scotland and Northern Ireland). They can be summarised as follows:

Air quality

- Statutory Instrument 1989 No 317, Clean Air, The Air Quality Standards Regulations 1989 gives limit values in air for nitrogen dioxide (any emission from the process should not result in a breach of this standard beyond the site boundary), sulphur dioxide and suspended particulates.
- Environmental Protection, The Air Quality Regulations 1997.
- Statutory Instrument 2000 No.928, Air Quality (England) Regulations 2000 gives air quality objectives to be achieved by:
 - 2005 for nitrogen dioxide
 - 2004 for SO2 and PM10
 - 2003 for CO, 1,3 butadiene and benzene
 - in two stages for lead by 2004 and 2008 respectively

Water quality

- Directive 76/464/EEC on Pollution Caused by Dangerous Substances Discharged to Water contains two lists of substances. List I relates to the most dangerous, and standards are set out in various daughter Directives. List II substances must also be controlled. Annual mean concentration limits for receiving waters for List I substances can be found in SI 1989/2286 and SI 1992/337 the Surface Water (Dangerous Substances Classification) Regulations. Values for List II substances are contained in SI 1997/2560 and SI 1998/389. Daughter Directives cover EQS values for mercury, cadmium, hexachlorocyclohexane, DDT, carbon tetrachloride, pentachlorophenol, aldrin, dieldrin, endrin, isodrin, hexachlorobenzene, hexachlorobutadiene, chloroform,1,2-dichloroethane, trichloroethane, perchloroethane and trichlorobenzene.
- Other waters with specific uses have water quality concentration limits for certain substances. These are covered by the following Regulations:
 - SI 1991/1597 Bathing Waters (Classification) Regulations
 - SI 1992/1331 and Direction 1997 Surface Waters (Fishlife) (Classification) Regulations
 - SI 1997/1332 Surface Waters (Shellfish) (Classification) Regulations
 - SI 1996/3001 The Surface Waters (Abstraction and Drinking Water) (Classification) Regulations

Future likely changes include:

- Some air quality and water quality standards may be replaced by new ones in the near future.
- The SED on the limitation of emissions of VOCs due to the use of organic solvents in certain activities and installations.

Other standards and obligations

Those most frequently applicable to most sectors are:

- Hazardous Waste Incineration Directive
- Waste Incineration Directive.
- Large Combustion Plant Directive.
- Reducing Emissions of VOCs and Levels of Ground Level Ozone: a UK Strategy (published by the Department of the Environment in October 1993. It sets out how the Government expects to meet its obligations under the UNECE VOCs Protocol to reduce its emissions by 30% (based on 1988 levels) by 1999, including the reductions projected for the major industrial sectors).
- Water Quality Objectives assigned water quality objectives to inland rivers and water courses (ref. Surface (Rivers Ecosystem) Classification).

Emissions Inventory Emission benchmarks

- The UNECE convention on long-range transboundary air pollution (negotiations are now underway which could lead to a requirement further to reduce emissions of NO_X and VOCs. A requirement to further reduce SO2 emissions from all sources has been agreed. The second Sulphur protocol (Oslo, 1994) obliges the UK to reduce SO2 emissions by 80% (based on 1980 levels) by 2010).
- The Montreal Protocol.
- The Habitats Directive (see Section 4.3).
- Sulphur Content of Certain Liquid Fuels Directive 1999/32/EC (from 1 January 2003, the sulphur content of heavy fuel oil must not exceed 1% except when it is burnt in plants fitted with SO2 abatement equipment. Sulphur levels in gas oil must not exceed 0.2% from 1 July 2000, and 0.1% from the start of 2008.)

3.2.4 Units for benchmarks and setting limits in permits

Releases can be expressed in terms of:

- "concentration" (for example mg/l or mg/m³), which is a useful day-to-day measure of the effectiveness of any abatement plant and is usually measurable and enforceable The total flow must be measured/controlled as well
- "specific mass release" (for example, kg/ product or input or other appropriate parameter), which
 is a measure of the overall environmental performance of the plant (including the abatement plant)
 compared with similar plants elsewhere
- "absolute mass release" (for example, kg/hr, t/yr), which relates directly to environmental impact

When endeavouring to reduce the environmental impact of an installation, its performance against each of these levels should be considered, as appropriate to the circumstances, in assessing where improvements can best be made.

When setting limits in Permits, the most appropriate measure will depend on the purpose of the limit. It may also be appropriate to use surrogate parameters, which reflect optimum environmental performance of plant as the routine measurement, supported by less frequent check-analyses on the final concentration. Examples of surrogate measures would be the continuous measurement of conductivity (after ion-exchange treatment) or total carbon (before a guard-column in activated carbon treatment) to indicate when regeneration or replacement is required.

The emission level figures given in this chapter are based on average figures, not on maximum, shortterm peak values, which could be expected to be higher. The emission levels given are based on a typical averaging period of not less than 30 minutes and not greater than 24 hours.

3.2.5 Statistical basis for benchmarks and limits in permits

Conditions in Permits can be set with percentile, mean or median values over annual, monthly or daily periods, which reflect probable variation in performance. In addition, absolute maxima can be set.

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Emission benchmarks

Where there are known failure modes, which will occur even when applying BAT, limits in Permits may be specifically disapplied, but with commensurate requirements to notify the Regulator and to take specific remedial action.

For water: UK benchmarks or limits are most frequently 95 percentile concentrations or absolute concentrations, (with flow limited on a daily average or maximum basis).

For air: benchmarks or limits are most frequently expressed as daily averages or, typically 95 percent of hourly averages.

3.2.6 Reference conditions for releases to air

The reference conditions of substances in releases to air from point-sources are:

- temperature 0 °C (273K)
- pressure 101.3 kPa
- no correction for water vapour or oxygen

To convert measured values to reference conditions, see the **Monitoring Guidance** for more information.

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4 Impact

4.1 Impact assessment

The Operator should assess that the emissions resulting from the proposals for the activities/installation will provide a high level of protection for the environment as a whole, in particular having regard to EQS etc, revisiting the techniques in Section 2 as necessary. The use of IPPC Environmental Assessments for BAT, and the IPPC Environmental Assessments for BAT software tool, and the other tools on the Application CD, will lead the Applicant through the process.

The depth to which the impact assessment should go should be discussed with the Regulator. For some low risk sites the requirements may be reduced.

Indicative BAT requirements for impact assessment (Sheet 1 of 2) Provide an assessment of the potential significant environmental effects (including transboundary effects) of the foreseeable emissions.

- 1 Provide a description, including maps as appropriate, of the receiving environment to identify the receptors of pollution. The extent of the area may cover the local, national and international (for example, transboundary effects) environment as appropriate.
- 2 Identify important receptors, which may include: areas of human population including noise or odour-sensitive areas, flora and fauna (that is, Habitat Directive sites, special areas of conservation, Sites of Special Scientific Interest (SSSI or in Northern Ireland ASSI) or other sensitive areas), soil, water, that is groundwater (water below the surface of the ground in the saturation zone and in direct contact with the ground and subsoil) and watercourses (for example, ditches, streams, brooks, rivers), air, including the upper atmosphere, landscape, material assets and the cultural heritage.
- 3 Identify the pathways by which the receptors will be exposed (where not self-evident).
- 4 Carry out an assessment of the potential impact of the total emissions from the activities on these receptors. IPPC Environmental Assessments for BAT provides a systematic method for doing this and will also identify where modelling needs to be carried out, to air or water, to improve the understanding of the dispersion of the emissions. The assessment will include comparison (see IPPC: A Practical Guide) with:
 - community EQS levels
 - · other statutory obligations
 - non-statutory obligations
 - environmental action levels (EALs) and the other environmental and regulatory parameters defined in IPPC Environmental Assessments for BAT
- 5 In particular it will be necessary to demonstrate that an appropriate assessment of vent and chimney heights has been made to ensure that there is adequate dispersion of the minimised emission(s) to avoid exceeding local ground-level pollution thresholds and limit national and transboundary pollution impacts, based on the most sensitive receptor, be it human health, soil or terrestrial ecosystems.

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Indicative BAT requirements for impact assessment (Sheet 2 of 2) Provide an assessment of the potential significant environmental effects (including transboundary effects) of the foreseeable emissions.

- 6 Where appropriate, the Operator should also recognise the chimney or vent as an emergency emission point and understand the likely behaviour. Process upsets or equipment failure giving rise to abnormally high emission levels over short periods should be assessed. Even if the Applicant can demonstrate a very low probability of occurrence, the height of the chimney or vent should nevertheless be set to avoid any significant risk to health. The impact of fugitive emissions can also be assessed in many cases.
- 7 Consider whether the responses to Sections 2 and 3 and this assessment adequately demonstrate that the necessary measures have been taken against pollution, in particular by the application of BAT, and that no significant pollution will be caused. Where there is uncertainty about this, the measures in Section 2 should be revisited as appropriate to make further improvements.
- 8 Where the same pollutants are being emitted by more than one permitted activity on the installation, the Operator should assess the impact both with and without the neighbouring emissions.

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4.2 Waste Management Licensing Regulations

Indicative BAT requirements for waste management licensing regulations Explain how the information provided in other parts of the application also demonstrates that the requirements of the relevant objectives of the Waste Management Licensing Regulations 1994 have been addressed, or provide additional information in this respect.

- In relation to activities involving the disposal or recovery of waste, the Regulators are required to exercise their functions for the purpose of achieving the relevant objectives as set out in Schedule 4 of the Waste Management Licensing Regulations 1994. (For the equivalent Regulations in Scotland and Northern Ireland, see Appendix 2.)
- 2 The relevant objectives, contained in paragraph 4, Schedule 4 of the Waste Management Licensing Regulations 1994 (SI 1994/1056 as amended) are extensive, but will only require attention for activities that involve the recovery or disposal of waste. Paragraph 4 (1) is as follows:
 - ensuring the waste is recovered or disposed of without endangering human health and without using process or methods which could harm the environment and in particular without:
 - risk to water, air, soil, plants or animals or
 - causing nuisance through noise or odours or
 - adversely affecting the countryside or places of special interest
 - · implementing, as far as material, any plan made under the plan-making provisions
- 3 The application of BAT is likely to already address risks to water, air, soil, plants or animals, odour nuisance and some aspects of effects on the countryside. It will, however, be necessary for the Operator briefly to consider each of these objectives individually and provide a comment on how they are being addressed by your proposals. It is also necessary to ensure that any places of special concern that could be affected, such as SSSIs, are identified and commented upon although, again, these may have been addressed in your assessment for BAT, in which case a cross-reference may suffice.
- 4 Operators should identify any development plans made by the local planning authority, including any waste local plan, and comment on the extent to which the proposals accord with the contents of any such plan (see Section 2.6).

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4.3 The Habitats Regulations

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Indicative BAT requirements for the habitats regulations

Provide an assessment of whether the installation is likely to have a significant effect on a European site in the UK and, if it is, provide an assessment of the implications of the installation for that site, for the purpose of the Conservation (Natural Habitats etc.) Regulations 1994 (SI 1994/2716)

- An application for an IPPC Permit will be regarded as a new plan or project for the 1 purposes of the Habitats Regulations (for the equivalent Regulations in Scotland and Northern Ireland see Appendix 2). Therefore, Operators should provide an initial assessment of whether the installation is likely to have a significant effect on any European site in the UK (either alone or in combination with other relevant plans or projects) and, if so, an initial assessment of the implications of the installation for any such site. The application of BAT is likely to have gone some way towards addressing the potential impact of the installation on European sites and putting into place techniques to avoid any significant effects. The Operator should provide a description of how the BAT assessment has specifically taken these matters into account, bearing in mind the conservation objectives of any such site.
- 2 European sites are defined in Regulation 10 of the Habitats Regulations to include Special Areas of Conservation (SACs); sites of community importance (sites that have been selected as candidate SACs by member states and adopted by the European Commission, but which are not yet formally classified); and Special Protection Areas (SPAs). It is also Government policy (set out in PPG 9 on nature conservation) that potential SPAs and candidate SACs should be considered to be European sites for the purposes of Regulation 10.
- 3 Information on the location of European sites and their conservation objectives is available from:
 - English Nature (01733 455000), http://www.english-nature.org.uk
 - Countryside Council for Wales (01248 385620), http://www.ccw.gov.uk
 - Scottish Natural Heritage (0131 447 4784), http://www.snh.org.uk
 - Joint Nature Conservation Committee (01733 866852), http://www.jncc.gov.uk
 - Environment and Heritage Service, Northern Ireland, http://www.ehsni.gov.uk
- 4 The Regulator will need to consider the Operator's initial assessment. If it concludes that the installation is likely to have a significant effect on a European site, then the Regulator will need to carry out an "appropriate assessment" of the implications of the installation in view of that site's conservation objectives. The Regulations impose a duty on the Regulator to carry out these assessments, so it cannot rely on the Operator's initial assessments. Therefore the Regulator must be provided with any relevant information upon which the Operator's assessment is based.
- 5 Note that in many cases the impact of the Habitats Regulations will have been considered at the planning application stage, in which case the Regulator should be advised of the details.

References

For a full list of available Technical Guidance see Appendix A of the Guide for Applicants or visit the Environment Agency Website http://www.environment-agency.gov.uk. Many of the references below are being made available free of charge for viewing or download on the Website. The same information can also be accessed via the SEPA web site http://www.sepa.org.uk, or the NIEHS web site www.ehsni.gov.uk. Most titles will also be available in hard copy from The Stationery Office (TSO). Some existing titles are not yet available on the Website but can be obtained from TSO.

- Ref 1 IPPC Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry European Commission http://eippcb.jrc.es
- Ref 2 The Pollution Prevention and Control Act (1999) (www.hmso.gov.uk).
- Ref 3 The Pollution Prevention and Control Regulations (SI 2000 No. 1973) (www.hmso.gov.uk).
- Ref 4 *IPPC: A Practical Guide* (for England and Wales) (or equivalents in Scotland and Northern Ireland) www.defra.gov.uk/environment/ppc/ippcguide/index.htm
- Ref 5 Guidance for applicants
 - *IPPC Part A(1) Installations: Guide for (Applicants England and Wales)* (includes Preparation of a Site Report in a Permit Application) (EA website).

• PPC Part A Installations: Guide for Applicants (Scotland) (Guidance for SEPA staff on land and groundwater considerations) Guidance for SEPA staff on land and groundwater considerations

- IPPC Regulatory Guidance Series No.5 Interpretation of "Installation" in the PPC Regulations
- www.environment-agency.gov.uk
- Ref 6 Assessment methodologies:
 - E1 BPEO Assessment Methodology for IPC
 - IPPC Environmental Assessments for BAT H1
- Ref 7 Waste minimisation support references

 Environment Agency web site. Waste minimisation information accessible via: www.environmentagency.gov.uk/subjects/waste/131528

• Waste Minimisation – an environmental good practice guide for industry (helps industry to minimise waste and achieve national environmental goals). Available free to companies who intend to undertake a waste reduction programme (tel: 0345 33 77 00)

• *Profiting from Pollution Prevention – 3Es methodology* (emissions, efficiency, economics). Video and A4 guide aimed at process industries. Available from Environment Agency, North East region (tel: 0113 244 0191, ask for Regional PIR)

• *Waste Minimisation Interactive Tools (WIMIT)*. Produced in association with Envirowise and the BOC Foundation (a software tool designed for small and medium businesses.). Available free from The Environmental Helpline (tel: 0800 585794)

• *ENVIROWISE*. A joint DTI/DEFRA programme, with over 200 separate case studies, good practice guides, leaflets, flyers, software tools and videos covering 12 industry sectors, packaging, solvents and the generic areas of waste minimisation and cleaner technology. ENVIROWISE is accessible via a FREE and confidential helpline (tel: 0800 585794) or via the web site www.envirowise.gov.uk

 Increased Profit Through Improved Materials Additions: Management/Technical Guide, ENVIROWISE, GG194/195

• *Waste Management Information Bureau*. The UK's national referral centre for help on the full range of waste management issues. It produces a database called Waste Info, which is available for on-line searching and on CD-ROM. Short enquiries are free (tel: 01235 463162)

• *Waste Minimisation* – Institution of Chemical Engineers Training Package E07. Basic course which contains guide, video, slides, OHPs etc. (tel: 01788 578214)

• *BIO-WISE* - *profiting through industrial biotechnology.* A DTI programme providing free advice and information about how biotechnology can be used within manufacturing industry. Case studies, guides website and Helpline 0800 432100. **dti.gov.uk/biowise** (leather guide GG237 and case study 11

- Ref 8 Water efficiency references:
 - Simple measures restrict water costs, ENVIROWISE, GC22
 - · Effluent costs eliminated by water treatment, ENVIROWISE, GC24
 - · Saving money through waste minimisation: Reducing water use, ENVIROWISE, GG26
 - ENVIROWISE Helpline 0800 585794

 Optimum use of water for industry and agriculture dependent on direct abstraction: Best practice manual. R&D technical report W157, Environment Agency (1998), WRc Dissemination Centre, Swindon (tel: 01793 865012)

- Cost-effective Water Saving Devices and Practices ENVIROWISE GG067
- Water and Cost Savings from Improved Process Control ENVIROWISE GC110
- Tracking Water Use to Cut Costs ENVIROWISE GG152
- Ref 9 Releases to air references:
 - BREF on Waste Water and Waste Gas Treatment.
 - A1 Guidance on effective flaring in the gas, petroleum etc. industries, 1993, ISBN 0-11-752916-8

A2 Pollution abatement technology for the reduction of solvent vapour emissions, 1994, £5.00, 0-11-752925-7

- A3 Pollution abatement technology for particulate and trace gas removal, 1994, £5.00, 0-11-752983-4
- Part B PG1/3 Boilers and Furnaces 20-50 MW net thermal input (ISBN 0-11-753146-4-7)
- Part B PG1/4 Gas Turbines 20-50 MW net thermal input (ISBN 0-11-753147-2
- Ref 10 Releases to water references
 - BREF on Waste Water and Waste Gas Treatment
 - A4 Effluent Treatment Techniques, TGN A4, Environment Agency, ISBN 0-11-310127-9 (EA website)

• Pollution Prevention Guidance Note – Above-ground oil storage tanks, PPG 2, Environment Agency, gives information on tanks and bunding which have general relevance beyond just oil (EA website)

• Construction of bunds for oil storage tanks, Mason, P. A, Amies, H. J, Sangarapillai, G. Rose, Construction Industry Research and Information Association (CIRIA), Report 163, 1997, CIRIA, 6 Storey's Gate, Westminster, London SW1P 3AU. Abbreviated versions are also available for masonry and concrete bunds (www.ciria.org.uk on-line purchase)

- Policy and Practice for the Protection of Groundwater (PPPG) (EA website)
- Choosing Cost-effective Pollution Control ENVIROWISE GG109
- Cost-effective Separation Technologies for Minimising Wastes and Effluents ENVIROWISE GG037
- Cost-effective Membrane Technologies for Minimising: Wastes and Effluents ENVIROWISE GG044
- Ref 11 Waste management references

• Investigation of the criteria for, and guidance on, the landspreading of industrial wastes – final report to the DEFRA, the Environment Agency and MAFF, May 1998

Ref 12 Energy references

• (Interim) Energy Efficiency Guidance, (available as draft Horizontal Guidance Note IPPC H2) (www.environment-agency.gov.uk)

Ref 13 COMAH guides

• A Guide to the Control of Major Accident Hazards Regulations 1999, Health and Safety Executive (HSE) Books L111, 1999, ISBN 0 07176 1604 5

• Preparing Safety Reports: Control of Major Accident Hazards Regulations 1999, HSE Books HS(G)190, 1999

• Emergency Planning for Major Accidents: Control of Major Accident Hazards Regulations 1999, HSE Books HS(G)191, 1999

• Guidance on the Environmental Risk Assessment Aspects of COMAH Safety Reports, Environment Agency, 1999 (EA website)

• Guidance on the Interpretation of Major Accidents to the Environment for the Purposes of the COMAH Regulations, DEFRA, 1999, ISBN 753501 X, available from the Stationery Office

- Ref 14 Monitoring Guidance
 - MCERTS approved equipment link via http://www.environment-agency.gov.uk/business/mcerts

• *M1* Sampling facility requirements for the monitoring of particulates in gaseous releases to atmosphere, March 1993, £5.00, ISBN 0-11-752777-7

• M3 Standards for IPC Monitoring Part 1: Standards, organisations and the measurement infrastructure, August 1995, £11.00, ISBN 0-11-753133-2

• M4 Standards for IPC Monitoring Part 2: Standards in support of IPC Monitoring, revised 1998

Direct Toxicity Assessment for Effluent Control Technical Guidance (2000), UKWIR 00/TX/02/07

- Ref 15 Noise references:
 - H3 Horizontal Guidance for Noise Part 1 Regulation and Permitting
 - H3 Horizontal Guidance for Noise Part 2 Assessment and Control
- Ref 16 Closure references

- Working at Construction and Demolition-sites (PPG 6) (EA website)
- Ref 17 Air Dispersion

• *Guidelines on Discharge Stack Heights for Polluting Emissions,* HMIP Technical Guidance Note (Dispersion) D1, 1993, ISBN 0-11-752794-7 www.tso.co.uk/bookshop; (or www.environment-agency.gov.uk for summary only)

- Ref 18 Fire Fighting
 - BS 5908: Code of Practice for Fire Precautions in the Chemical and Allied Industries

• *PPG 18 - Managing Fire-water and major spillages,* Environment Agency Pollution Prevention Guidance Note (see Ref 10)

Ref 19 Volatile Organic Compounds

• The Categorisation of Volatile Organic Compounds, 1995 HMIP Research Report No DOE/HMIP/RR/95/ 009 (www.environment-agency.gov.uk)

Ref 20 Environment Agency Technical Guidance for the previous (IPC) regulatory regime

• Large Volume Organic Chemicals, IPC S2 4.01, Environment Agency, 1999, ISBN 0-11-310153-8 www.tso.co.uk/bookshop or www.environment-agency.gov.uk

Abbreviations

BAT	Best Available Techniques – see IPPC A Practical Guide or the Regulations for further definition
BAT Criteria	The criteria to be taken into account when assessing BAT, given in Schedule 2 of the PPC Regulations
BOD	Biochemical Oxygen Demand
BREF	BAT Reference Document
CEM	Continuous Emissions Monitoring
СНР	Combined heat and power plant
COD	Chemical Oxygen Demand
ELV	Emission Limit Value
EMS	Environmental Management System
EQS	Environmental Quality Standard
ETP	Effluent treatment plant
FOG	Fat Oil Grease
ITEQ	International Toxicity Equivalents
MCERTS	Monitoring Certification Scheme
NIEHS	Northern Ireland Environment and Heritage Service
SAC	Special Areas of Conservation
SECp	Specific Energy consumption
SEPA	Scottish Environment Protection Agency
SPA	Special Protection Area
TSS	Suspended solids
тос	Total Organic Carbon
VOC	Volatile organic compounds

Appendix 1: Some common monitoring and sampling methods

Table 4.1: Measurement methods for common substances to water

Determinand	Method	Detection limit Uncertainty	Valid for range mg/l	Standard
Suspended solids	Filtration through glass fibre filters	1 mg/l 20%	10-40	ISO 11929:1997, EN872 - Determination of suspended solids
COD	Oxidation with di-chromate	12 mg/l 20%	50-400	ISO 6060: 1989, Water Quality - Determination of chemi- cal oxygen demand
BOD5	Seeding with micro- organisms and measurement of oxygen content	2 mg/l 20%	5-30	ISO 5815: 1989, Water Quality Determination of BOD after 5 days, dilution and seeding method EN 1899 (BOD 2 Parts)
AOX	Adsorption on acti- vated carbon and combustion	 20%	0.4 - 1.0	ISO 9562: 1998, EN1485 - Determination of adsorbable organically bound halogens.
Tot P				BS 6068: Section 2.28 1997, Determination of phospho- rus –ammonium molybdate spectrometric method
Tot N				BS 6068: Section 2.62 1998, Determination of nitrogen Part 1 Method using oxidative digestion with peroxydi- sulphate, BS EN ISO 11905
рН				SCA The measurement of electric conductivity and the determination of pH, ISBN 0117514284
Turbidity				SCA Colour and turbidity of waters 1981, ISBN 0117519553 EN 27027:1999
Flow rate	Mechanical ultra- sonic or electromag- netic gauges			SCA Estimation of Flow and Load, ISBN 011752364X
Temperature				
ТОС				SCA The Instrumental Determination of Total Organic Carbon and Related Determinants 1995, ISNB 0117529796 EN 1484:1997
Fatty acids				Determination of Volatile Fatty Acids in Sewage Sludge 1979, ISBN 0117514624
Metals				BS 6068: Section 2.60 1998, Determination of 33 ele- ments by inductively coupled plasma atomic emission spectroscopy
Chlorine				BS6068: Section 2.27 1990, Method for the determina- tion of total chlorine: iodometric titration method
Chloroform Bromoform				BS 6068: Section 2.58, Determination of highly volatile halogenetaed hydrocarbons – Gas chromatographic methods
Dispersants Surfactants Anionic Cationic Non-ionic				SCA Analysis of Surfactants in Waters, Wastewaters and Sludges, ISBN 01176058 EN 903:1993 (Used for ani- onic surfactants)
Pentachloro- Phenol				BS5666 Part 6 1983, Wood preservative and treated tim- ber quantitative analysis of wood preservatives contain- ing pentachlorophenol EN 12673:1997 (used for chlorophenol and polychlorinated phenols)

Table 4.1: Measurement methods for common substances to water

Determinand	Method	Detection limit Uncertainty	Valid for range mg/l	Standard
Formaldehyde				SCA The determination of formaldehyde, other volatile aldehydes and alcohols in water
Phosphates and nitrates				BS 6068: Section 2.53 1997, Determination of dissolved ions by liquid chromatography
Sulphites and sulphates				BS 6068: Section 2.53 1997, Determination of dissolved ions by liquid chromatography
Ammonia				BS 6068: Section 2.11 1987, Method for the determina- tion of ammonium: automated spectrometric method
Grease and oils	IR absorption	0.06 mg/kg		SCA The determination of hydrocarbon oils in waters by solvent extraction IR absorption and gravimetry, ISBN 011751 7283

Table 4.2: Measurement methods for air emissions

Determinand	Method	Av'ging time Detection limit Uncertainty	Compliance criterion	Standard
Formaldehyde	Impingement In 2,4 dinitro-phenyl- Hydrazine HPLC	1 hour 1 mg/m ³ 30%	Average of 3 consecutive samples below specified limit	US EPA Method 316 Method specific to formaldehyde.
Ammonia	FTIR or Ion Chromatogra- phy	1 hour 0.5mg/m ³ 25%		US EPA Method 320 for extractive instruments. US EPA Method 26 for wet chemistry.
VOCs	Speciated - Adsorption Thermal Desorption GCMS	1 hour 0.1 mg/m ³ 30%		BS EN 1076:1997 Workplace atmos- pheres. Pumped sorbent tubes for the determination of gases and vapours. Requirements and test methods.
	Total Organic Car- bon	1 hour 0.4 mg/m ³ calculated	Continuous or spot check	BS EN 12619:1999. Determination of the mass concentration of total gaseous organic carbon at low concentrations in flue gases – continuous flame ionisation method.3
Chloroform	Absorption on acti- vated carbon sol- vent extraction. GC analysis	1 hour 1 mg/m ³ 20%	Average of 3 consecutive samples below specified limit	MDHS 28 Chlorinated hydrocarbon sol- vent vapours in air (modified)
Oxides of Sulphur	UV fluorescence Automatic ana- lyser	1 hour 1 ppm 10%	95% of hourly averages over a year below specified limit	BS6069 Section 4.4 :1993 (ISO 7935) Stationary source emissions-determina- tion of mass concentrations of sulphur dioxide4.
	Wet sampling train Ion chromatogra- phy	1 hour 1 mg/m ³ 25%	Average of 3 consecutive samples below specified limit	BS6069 Section 4.1:1998 (ISO 7934) Method for the determination of the mass concentration of sulphur dioxide- hydrogen peroxide/barium perchlorate method
Hydrogen Chloride	Wet sampling 3 analytical methods	30 minute mini- mum 0.2 mg/m ³ calculated	One test	BS EN 1911:Parts 1-3:1998 Manual method of determination of HCI
Particulate matter	Extractive – sample train	3 minutes per point 5 mg/m ³ 10%	One test	BS EN 13284-1:2002 Determination of low range mass concentration of dust — Part 1: Manual gravimetric method.

Table 4.2: Measurement methods for air emissions

Determinand	Method	Av'ging time Detection limit Uncertainty	Compliance criterion	Standard
	Continuous – Automatic ana- lyser	Continuous N/A 10%	Continuous	BS ISO 10155:1995Automated Monitor- ing of mass concentrations of particles – performance characteristics, test meth- ods and specifications.
PCDD/F	Extractive – Sample train GC/MS	4 hour minimum 8 hour maximum 0.1 ng I-TEQ/m ³ calculated		BS EN 1948:1997 determination of the mass concentration of PCDD/F

Measurement uncertainty is defined as total expanded uncertainty at 95% confidence limit calculated in accordance with the Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st Ed., Geneva, Switzerland, ISO 1993.

See also Monitoring Guidance

Appendix 2: Equivalent legislation in Wales, Scotland & Northern Ireland

The legislation referred to in the text is that for England. The following are the equivalents for Scotland, Wales and Northern Ireland.

Table 4.3: Equivalent legislation

England	Wales	Scotland	Northern Ireland
PPC Regulations (Eng- land and Wales) 2000	As England	PPC (Scotland) Regula- tions 2000, SI 200/323	To be prepared
SI:1994 1056: Waste Man- agement Licensing Regu- lations	As England	As England	To be prepared
The Water Resources Act 1991	As England	COPA 1974 (S30A-30E equiv to Part III WRA91): Natural Herit- age (Scotland) Act 1991 (Part II equiv to Part I WRA91)	The Water (NI) Order 1999
SI 1989 No.317: Clean Air, The Air Quality Standards Regulations 1989 SI 1995 No. 3146: The Air Quality Standards (Amendments) Regula- tions 1995	As England	As England	SR 1990 No.145: The Air Quality Standards Regulations (Northern Ireland) 1990 SR1996 No.23: The Air Quality Standards (Amendments) Regula- tions (Northern Ireland) 1996
SI 2000 No.928: The Air Quality (England) Regula- tions 2000	SI 2000 No.1940 (W.138): The Air Quality (Wales) Regulations 2000	SSI 2000/97: The Air Quality (Scotland) Regu- lations	No NI equivalent
SI 2001 No.2315: The Air Quality Limit Values Regu- lations 2001	SI 2001 No.2683 (W.224): The Air Quality Limit Values (Wales) Regulations 2001	SSI 2001 No.224: The Air Quality Limit Values (Scotland) Regulations 2001	SI 2002 No.94: The Air Quality Limit Values (Northern Ireland) Regu- lations 2002
SI 1989 No 2286 and 1998 No 389: The Surface Water (Dangerous Sub- stances Classification) Regulations. (Values for List II substances are con- tained in SI 1997/2560 and SI 1998/389)	As England	SI 1990/126: Surface Water (Dangerous Sub- stances) (Classification) (Scotland) Regulations	Surface Waters (Danger- ous Substances) (Classi- fication) Regulations 1998. Statutory Rules of Northern Ireland 1998 No 397
SI 1991 No.1597: Bathing Waters (Classification) Regulations 1991	As England	SI 1991 No.1609: Bath- ing Waters (Classifica- tion) (Scotland) Regulations 1991	The Quality of Bathing Water Regulations (NI) 1993
SI 1997 No.1331: The Surface Waters (Fishlife) (Classification) Regula- tions 1997	As England	SI 1997 No.2471 (S.163): The Surface Waters (Fishlife) (Classi- fication) (Scotland) Reg- ulations 1997	The Surface Water (Fish- life) (Classification) Reg- ulations (NI) 1997
SI 1997 No.1332: The Surface Waters (Shellfish) (Classification) Regula- tions 1997	As England	SI 1997 No.2470 (S.162): The Surface Waters (Shellfish) (Clas- sification) (Scotland) Regulations 1997	The Surface Water (Shellfish) (Classifica- tion) Regulations (NI) 1997
SI 1994 No.2716: The Conservation (Natural Habitats, etc) Regulations	As England	As England	Conservation (Natural Habitats etc) Regulations (Northern Ireland) 1995

Table 4.3: Equivalent legislation

England	Wales	Scotland	Northern Ireland
SI 1999 No.743: Control of Major Accident Haz- ards Regulations (COMAH) 1999	As England	As England	SR 2000 No.93: Control of Major Accident Haz- ards Regulations (North- ern Ireland) 2000
SI 1998 No.2746: The Groundwater Regulations 1998	As England	As England	SR 1998 No.401. The Groundwater Regula- tions (Northern IrelandI) 1998

Appendix 3: Volatile Organic Compounds

Introduction

Volatile organic compounds (VOCs) are of serious environmental concern because of the harmful or offensive properties that they exhibit in varying degrees. These include:

- direct toxicity to human health and other eco-systems
- contribution to photochemical ozone creation at ground level with consequent harmful effects
- destruction of stratospheric ozone
- contribution to global climate change; and
- sensory effects such as malodour

The harmfulness of VOCs varies greatly, not only because the individual and combined significance of these properties exhibits wide variation between substances, but also because it is dependent on the presence of the substance in the environment. This is related to mass release rate and subsequent dispersion and to the environmental persistence and fate of the substance under prevailing conditions.

Categorisation

In order to assess BAT for processes that release VOCs, it is necessary to categorise VOCs according to their harmfulness.

Substances such as benzene, vinyl chloride and 1,2- dichloroethane pose serious health risks to humans and are regarded as highly harmful. These are given individual, very low achievable levels of emission in guidance.

Some other VOCs carry a lesser but still significant health risk or may contribute substantially to photochemical ozone creation or stratospheric ozone destruction or global warming. These are regarded as of medium harmfulness and are allocated to Class A. They will include the substances listed in the Montreal Protocol, the phase-out of which is covered by EC Regulations 594/91, 3952/92, 2047/93 and 3093/94.

The remaining majority of VOCs are of low harmfulness but are also substances whose release should be prevented or minimised. These are allocated to Class B.

Odorous VOCs may be offensive at extremely low concentrations and this property may indicate the need for very tight control of a substance that would otherwise be categorised as of low harmfulness.

The research report "The Categorisation of Volatile Organic Compounds" (DOE/HMIP/RR/95/009) provides a method of categorisation, information on the properties of some 500 VOCs and a summary table of resulting categorisations.

In seeking to categorise a VOC, first search the summary table of categorisations. If the VOC is not included, the method and decision tree given in the research report should be used to arrive at a conclusion supported as well as possible by information from established sources. These include the Registry of Toxic Effects of Chemicals, the "CHIP" list, the Montreal Protocol and Sax' Dangerous Properties of Industrial Materials.

Knowledge of the harmful effects of VOCs is developing and there may be occasional differences of experts' opinions on the precise interpretation of information. In these few instances, it will be prudent to adopt the more cautious view.

Achievable Benchmark Levels

The levels of emission that can be achieved are dependent on factors that include the process itself, the VOC concerned and the abatement method used.

Where possible, process- and substance-specific achievable levels of release are given in Table 3.1 of this Note. However, in the absence of sufficient information or where it is agreed that an assessment is not possible, the following guidelines may be used to provide a practical approach to setting limits.

• The benchmark release concentrations given below should be aimed for where the following mass release limits are exceeded:

Total Class A - 100 g/h Total Class B (expressed as carbon) - 2 kg/h

- but emissions below these mass emission levels may not be trivial, and so may still require controls and the setting of appropriate release limits.

- Highly harmful VOCs pose major human health risks and have individual guidance levels given in Table 3.1 of this Note.
- For Class A compounds, BATabatement techniques should achieve a benchmark release level of 20 mg/m3 for continuous emissions.
- Some VOCs cause significant malodour problems even at very low concentrations after dispersion, and limits lower than Class A compounds may be required.
- Class B compounds are those of low environmental harmfulness such as acetone and toluene and the Class B benchmark level has been set at 75 mg/m3 (expressed as carbon) based on abatement techniques involving adsorption with activated carbon.
- For mixed streams the release level may be calculated by summing the class levels multiplied by their respective mass fractions.
- The use of a release concentration limit is not normally appropriate in the case of a release from an air-deficient saturated vapour space such as storage tanks for solvents or process vessels. An approach based on limiting total mass released or mass per unit of production is likely to be more effective.
- In some processes, the VOCs released to air may well consist of partial oxidation products rather than defined compounds that can be classified as above. In such cases an approach based on a TOC release concentration is likely to be more appropriate.

Appendix 4: Groundwater Regulations 1998. Schedule of listed substances and recommendations for List I

List I

- 1.-(1) Subject to the sub paragraph below, a substance is in List I if it belongs to one of the following families or groups of substances:
 - (a) organohalogen compounds and substances that may form such compounds in the aquatic environment
 - (b) organotin compounds
 - (c) substances that possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment (including substances that have those properties that would otherwise be in List II)
 - (d) mercury and its compounds
 - (e) cadmium and its compounds
 - (f) mineral oils and hydrocarbons
 - (g) cyanides.
- 1.-(2) A substance is not in List I if it has been determined by the Regulator to be inappropriate to List I on the basis of a low risk of toxicity, persistence and bioaccumulation.

List II

- 2.-(1) A substance is in List II if it could have a harmful effect on groundwater and it belongs to one of these families or groups of substances:
 - (a) the following metalloids and metals and their compounds:

zinc	tin	copper
barium	nickel	beryllium
chromium	boron	lead
uranium	selenium	vanadium
arsenic	cobalt	antimony
thallium	molybdenum	tellurium
titanium	silver	

- (b) biocides and their derivatives not appearing in List I
- (c) substances that have a harmful effect on the taste or odour of groundwater, and compounds liable to cause the formation of such substances in such water and to render it unfit for human consumption
- (d) toxic or persistent organic compounds of silicon, and substances that may cause the formation of such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances
- (e) inorganic compounds of phosphorus and elemental phosphorus
- (f) fluorides
- (g) ammonia and nitrates.
- 2.-(2) A substance is also in List 2 if:

(a) it belongs to one of the families or groups of substances set out in paragraph 1(1) above

- (b) it has been determined by the Regulator to be inappropriate to List I under paragraph 1(2); and
- (c) it has been determined by the Regulator to be in inappropriate to List II having regard to toxicity, persistence and bioaccumulation.
- 3.-(1) The Secretary of State or Scottish Ministers may review any decision of the Regulator in relation to the exercise of its powers under the paragraphs above.
- 3.-(2) The Secretary of State or Scottish Minister shall notify the Regulator of his decision following a review under List 1 sub paragraph 1 above and it shall be the duty of the Regulator to give effect to that decision.
- 4.- The Regulator shall from time to time publish a summary of the effect of its determinations under this Schedule in such manner as it considers appropriate and shall make copies of any such summary available to the public free of charge.

List of substances recommended to be confirmed as List I

- as recommended by the Joint Agency Groundwater Directive Advisory Group.

Aldrin	Diuron
Atrazine	Endosulfan
Azinphos-ethyl	Fenitrothion
Bromoxynil (as Bromoxynil-phenol)	Fenthion
Bromoxynil octanoate	Heptachlor
Cadmium	Hexachlorobenzene
2-Chloroaniline	Hexachlorobutadiene (HCBD)
Chlorobenzene	Hexachlorocyclohexane
Chlordane	Hexachloroethane
Chloro-2,4-dinitrobenzene	Hexachloronorbornadiene
Chlorfenvinphos	Hexaconazole
4-Chloro-3-methylphenol	3-lodo-2-proponyl n-butyl carbamate (IPBC)
Chloro-2-nitrobenzene	Linuron
Chloro-3-nitrobenzene	Malathion
Chloro-4-nitrobenzene	Mercury
2-Chlorophenol	Mevinphos
Chlorothalonil	Oxydemeton-methyl
2-Chlorotoluene	Parathion
a-Chlorotoluene	Parathion-methyl
Chlorpyrifos	Pentachlorobenzene
Coumaphos	Pentachloroethane
Cypermethrin	Pentachlorophenol (PCP)
DDT	Permethrin
Demeton	Propanil
Diazinon	Simazine
Dibutyl bis(oxylauroyl)tin	Tetrabutyltin
Dichlofluanid	1,2,4,5-Tetrachlorobenzene

Dichloroaniline	Tetrachloroethylene
1,2-Dichlorobenzene	Triazophos
1,3-Dichlorobenzene	Tributyl tin oxide (TBTO)
1,4-Dichlorobenzene	Tributyl-phosphate
Dichloronitrobenzene (all isomers)	Trichlorfon
2,4-Dichlorophenol	1,2,4-Trichlorobenzene
1,3-Dichloropropene	Trichloroethylene
Dichlorprop	Trichlorophenol (all isomers)
Dichlorvos	Trifluralin
Dicofol	Triphenyl tin oxide (TPTO)
Dieldrin	Triphenyl-phosphate
Dimethoate	