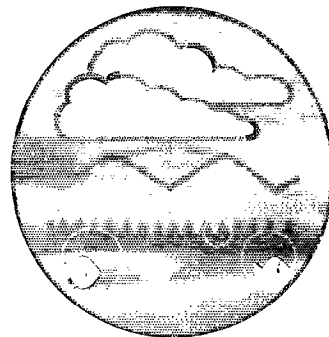
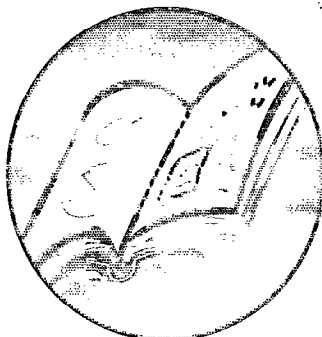
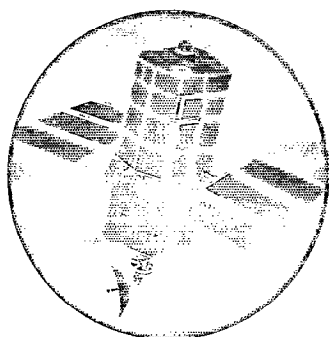


# Best Available Techniques in the Fine and Speciality Organic Chemical Sector



## Research and Development

Technical Report  
P163



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# Best Available Techniques in the Fine and Speciality Organic Chemical Sector

R&D Technical Report P163

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This report provides information on best available techniques for pollution control in speciality organic chemical processes. It includes costs of the techniques and economic information on the industry sub sectors. The report will be used in the revision of IPC process guidance on the relevant process.

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## EXECUTIVE SUMMARY

This study has been undertaken to underpin the preparation of an updated IPC Guidance Note for the Fine and Speciality Organic Chemical Sector (the Sector). The study has reviewed techniques for the prevention, minimisation and rendering harmless of releases from the sector and has identified those that presently constitute best available techniques (BAT).

The sector is characterised by its size, nearly one third of the approximately 2100 processes presently controlled under IPC fall within it, and the use of batch operations that leads to a diverse range of reaction chemistries, process units, products, raw materials and releases. These characteristics make it difficult to be prescriptive about BAT for the sector, particularly when discussing the more traditional, end-of-pipe, abatement techniques.

For this reason this study has developed the innovative concept of management and process techniques. Management techniques relate to systems and procedures. Process techniques relate to plant equipment and process units. Both management and process techniques place a much higher priority than abatement techniques on preventing and minimising releases at source. It is the major recommendation of this study that greater emphasis be placed on the use of management and process techniques in the sector.

There is no unique way of managing a process but there are still a number of areas that an inspector could expect to be addressed. A number of potential management techniques have been identified that will aid in this task. These include ensuring that there is a clear organizational structure and assignment of responsibility for complying with the authorisation. Maintenance should generally be based on a proactive rather than reactive philosophy. The key indicators of process performance should be identified and information regularly collected and considered on them. There should be a presumption that regular waste minimisation audits are undertaken. Environmental issues should be integrated into process and product design and development at the earliest possible stage. Staff should be made fully aware of the IPC authorisation and their contribution to achieving compliance with it. Training should be provided to staff whose work may have a significant impact on the environment. Robust systems should be in place for responding to, reporting and learning from incidents. Finally, wherever practicable, the true financial cost of releases should be assigned to the process and if possible process unit from which they originate. The use of voluntary standards for environmental management systems (EMS) should be encouraged.

Despite the diversity of the sector five basic unit processes have been identified that inspectors are likely to see at most processes and these can be used as a framework for the discussion of process techniques. These are storage/handling, plant systems/equipment, reaction, separation and purification. All of these unit processes can be designed, used and maintained in a manner that minimises releases, particularly those associated with fugitive losses of volatile organic compounds (VOCs) and the need to washdown between batches. An inspector could reasonably expect that a process operator understood the releases associated with the use of unit processes, that these releases had been prioritised for control and that, where necessary, process techniques had been used to prevent, minimise and render harmless releases. Process techniques include bunding storage tanks, isolating drainage systems from potential spills and ensuring that adequate retention capacity is available to deal with fire fighting water. Process equipment and systems (pumps, valves, over pressure systems etc.) should be selected on the

basis of the volume and nature of releases. Thus for large releases and/or substances that may be particularly harmful greater consideration will need to be given to the use of high integrity equipment that minimise leaks etc. Reaction, separation and purification units should be designed, operated and maintained to minimise leaks, maximise product yields and minimise the waste arisings from washing operations.

Notwithstanding the recommendation that greater emphasis be placed on management and process techniques, abatement techniques will continue to play an important role in the control of releases in this sector. A number of developments have taken place in air abatement techniques that are of relevance, in particular relating to VOCs. Catalytic oxidation is now a more robust technique than previously, less susceptible to poisoning, although the wide variations in flow, concentration and substances released characteristic of this sector may preclude its widespread use. Flameless thermal oxidation appears to address many of these potential problems and it may be expected that greater consideration be given to its use in the sector. Similarly cryogenic condensation appears to achieve very good release levels whilst minimising the creation of secondary pollutants. However, its high operating costs may preclude its use where liquid nitrogen is not used for some other purpose. Biological oxidation has also evolved rapidly as a technique, although again the fluctuations prevalent in the sector and the often harsh physical (temperature, pH) characteristics of many gas streams may limit its use.

Developments have also occurred in waste water techniques. However, it is a major recommendation of this study that greater consideration be given by the process operator to the initial characterisation of waste water arisings. This will aid prevention and minimisation at source as well as optimising subsequent treatment steps. To provide some structure for their discussion, waste water techniques have been divided into special (applied to individual streams that may be particularly toxic or odorous or have the potential for recovery), pre-treatment (relatively simple techniques used to prepare waste water for subsequent treatment), central (biological treatment or chemical coagulation) and polishing (targeted at the removal of recalcitrant substances not dealt with by earlier treatment) techniques, respectively. It could be expected that for most effluents some form of biological treatment may be appropriate. This may be provided on-site or by a sewage undertaker following discharge to sewer. More consideration should be given to the potential for isolating problematical waste streams and applying special techniques to them.

A wide range of abatement techniques are available in this and other sectors. To aid inspector's decision making, BAT for abatement techniques has often been translated into benchmark release levels. A number of potential problems with using benchmark release levels in this sector have been identified. In particular those associated with intermittent releases characteristic of batch operations, the complexity of the gas streams involved, the diversity of products/raw materials/releases and the lack of information from other countries and international bodies for this sector. No evidence could be found to justify tightening many of the benchmark release levels for air, although it is proposed that the levels for oxides of sulphur and nitrogen, respectively, be reduced from 300 to 200 mg/m<sup>3</sup>. Recommendations have been made for benchmark release levels for water, although these have generally been derived from less robust sources than those for air. In particular, the level proposed for COD should be applied with considerable caution.

This study has not considered in detail the potential implications for the sector of implementation of the IPPC Directive. However, it is apparent that the sector may be particularly amenable to IPPC considerations such as raw material, energy and water use.

A number of issues of particular importance to this sector were also considered. The control of releases of VOCs is considered to be by far the most important issue and has been addressed throughout the study. Dioxins do not appear to be a particularly important issue for this sector, although a few, very specific situations when they may be created have been identified. Endocrine disrupters and direct toxicity assessment are likely to be important issues for the sector in the future and close attention should be paid to them.

Economic assessment of the implications of BAT for the sector and individual processes is difficult. This reflects the diversity of markets that processes in this sector operate in. These cover the chemical, food, aerospace, fuel and construction sectors amongst others. A core of the process operators of the sector could be said to be dedicated batch chemical operations but even these companies sell their products so widely that they are dependent on the well being of the economy as a whole rather than a specific element of it.

Many of the companies operating in this sector are SMEs. Implementation of BAT may have a disproportionate impact on SMEs when compared to larger organizations and careful consideration should be paid to the economic constraints on them, for example the generally higher cost of capital. Attention should also be paid to the global nature of the markets that the sector operates in. Relatively high product costs means that transport costs are generally of low importance. Competition is therefore global and will include Far Eastern countries whose regulatory cost base is usually considerably lower than that in the UK. Investment is also highly mobile and at the moment UK companies in the sector are investing considerably more abroad than overseas companies are investing in the UK. Returns on capital employed and assets, respectively, are generally higher than the UK average, although this does reflect the higher perceived risk of investing in this sector. Notwithstanding these potential adverse impacts, financial analysis of the sector suggest that there is scope for further small to moderate investments in BAT across the sector.

Individual companies may of course differ from this sector 'average' and guidance is provided to inspectors on indicators of a process operator's ability to meet further investment requirements.

## **KEY WORDS**

Fine and speciality organic chemical, Best Available Techniques, integrated pollution control, management techniques, process techniques, abatement techniques.



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# 1. INTRODUCTION

## 1.1 Background to Study

This study reviews techniques to prevent, minimise and render harmless releases from processes operating in the fine and speciality chemical sector ('the sector'); specifically those covered by the integrated pollution control (IPC) regime in England and Wales.

Under the Environmental Protection Act 1990 (HMSO 1990), prescribed processes must apply for and operate within the conditions of an IPC authorisation. To assist in the implementation of the Act, Her Majesty's Inspectorate of Pollution (HMIP) (now incorporated into the environment Agency) issued Chief Inspector's Guidance Notes (CIGNs), recently renamed IPC Guidance Notes, for processes controlled under IPC authorisation. For the chemical sector, twenty-five IPC Guidance Notes were issued. The Agency recently announced that it intended to reduce the number of Guidance Notes for chemical processes to four and to provide Inspectors with updated and more targeted guidance which includes an assessment of the economic implications of utilising BAT. This revision of Guidance Notes coincides with the first four yearly review of authorisations in the chemical sector.

To support the revisions of guidance, the Agency has commissioned studies into **pollution** prevention and control in the chemical industry. These studies will underpin the preparation of new IPC Guidance Notes for the four sub-sectors of the chemical industry.

The report and associated Guidance Note covers most, but not all, processes found in the following Sections of the Environmental Protection (Prescribed Processes and Substances) Regulations 1991 (HMSO 1991):

- 4.2 (the manufacture and use of organic chemicals);
- 4.3 (acid processes);
- 4.4 (processes involving halogens);
- 4.7 (pesticide production); and
- 4.8 (pharmaceuticals).

Section 1.2, below, outlines the approach taken in preparing this report, whilst Section 1.3 briefly summarises the wider framework for environmental policy and legislation within which IPC fits.

For BAT, "available" means available world-wide, and so to provide guidance on BAT (in the revised IPC Guidance Notes) it has been necessary to assess the current techniques applied on a world-wide basis. Techniques have also been assessed in terms of their impact on the different environmental compartments to obtain information on the overall impact on the environment.

## 1.2 Report Structure

This report is structured as follows:

- Chapter One provides an introduction to the study and briefly describes the legislative and regulatory context within which it has been prepared;
- Chapter Two provides summary background information on the sector. For example, the number of processes involved, the chemical reactions utilised and the main sources of releases, substances involved and resulting environmental impacts;
- Chapter Three outlines the general approach that has been adopted for evaluating techniques;
- Chapter Four considers management techniques;
- Chapter Five considers process techniques;
- Chapter Six considers air abatement techniques;
- Chapter Seven considers waste water abatement techniques;
- Chapter Eight considers disposal to land abatement techniques;
- Chapter Nine briefly summarises techniques that are currently under development and that may be 'available' in the future;
- Chapter Ten considers the issue of benchmark release levels;
- Chapter Eleven briefly addresses the issues of BPEO and sustainability and their implications for the selection of BATNEEC in the sector;
- Chapter Twelve considers a number of issues that are of particular relevance to this sector;
- Chapter Thirteen provides the conclusions of the study;
- Appendix I is a catalogue of the techniques considered during this study;
- Appendix II provides further detail on the environmental issues relating to individual sub-sectors covered by this study, in effect an expansion of Chapter 2;
- Appendix III assesses the economic implications of selecting and implementing BATNEEC.

### 1.3 Legislative framework

The Integrated Pollution Control (IPC) regime created under the Environmental Protection Act (EPA) 1990 provides a mechanism for the control of the environmental impacts associated with some of the most polluting processes in England and Wales. However, an IPC authorisation needs to be prepared and enforced within the context of a much wider legislative framework for the protection of the environment.

This section briefly summarises this legislative framework and its implications for the sector, of particular relevance are:

- authorisation conditions for routine and non-routine releases that are made directly and indirectly (via sewerage systems) need to be set within the context of any EQSs and higher level quality targets that have been set for the receiving waters;
- the Environment Agency's Groundwater Protection Policy needs to be considered when setting authorisation requirements for the delivery, handling and storage of raw materials, products and wastes under both routine and non-routine situations;
- international commitments to reduce the input of dangerous substances to the aquatic environment. The UK has made a number of such commitments in fora such as North Sea Conferences and the Oslo/Paris Commission (Osparcom). These commitments are to a large extent reflected in the prescribed substances defined under the EPA 90 but they may also be altered in future years. For example, Osparcom is developing a new mechanism for prioritising dangerous substances;
- although solid/liquid waste generation is covered under the IPC regime, the off-site disposal of such wastes is covered by other regulatory systems, in particular Part II of the EPA 90. Authorisations need to be prepared in the context of this system, with particular attention being paid to the Government's waste strategy (HMSO 1995), waste hierarchy and definition of special waste (HMSO 1996a), as well as the EU's proposed Directives on the Incineration of Hazardous Waste (COM 1997a) and the Landfilling of Waste (COM 1997b), respectively;
- Statutory Instrument 1997 No. 3043, Environmental Protection, The Air Quality Regulations 1997 gives air quality objectives to be achieved by 2005. In addition, the Government has made or is in the process of making commitments on an international level relating to reductions in the emissions of volatile organic compounds (VOCs), persistent organic compounds (POPs), certain heavy metals, gases contributing to global warming, certain metals, oxides of sulphur and oxides of nitrogen. Authorisations need to be prepared within the context of these commitments;
- the UK operates a comprehensive system for the protection of worker and public safety from the consequences of accidents at major industrial sites. Presently based on the CIMAH Regulations (HMSO 1984) and likely to be revised shortly with the introduction of the EU's Seveso II (COMAH) Directive (CEC 1996b) they are a major factor in reducing the potential impact of incidents on both human safety and environmental quality;

- the Land Use Planning system now takes into account the environmental impacts associated with development;
- whilst not statutory, voluntary environmental management standards (ISO 14001 (ISO 1996) and Emas (CEC 1993)) have been introduced.

## 2. CHEMICAL INDUSTRY BACKGROUND

This section provides an overview of the sector. In particular it covers:

- number of processes;
- the basic chemical engineering units that underpin these processes; and
- how individual sub-sectors may differ from these basic units and from each other.

### 2.1 Number of Processes

This study covers Sections 4.2, 4.3, 4.4, 4.7 and 4.8 of the Environmental Protection (Prescribed Processes and Substances) Regulations 1991 (SI 1991/472) (HMSO 1991). Figures for the number of processes in England and Wales covered by these sections of the Regulations are provided in Table 2.1. These figures are now relatively dated and should be treated with some caution.

**Table 2.1** Number of processes covered by this study

Section	Description	Number	Percentage of total
4.2a	The manufacture of styrene or vinyl chloride (including polymerisation and co-polymerisation)	94	10.11
4.2b	any process of manufacture involving the use of vinyl chloride	2	0.22
4.2c	the manufacture of acetylene, any aldehyde, amine, isocyanate, nitrile (any carboxylic acid or any anhydride of carboxylic acid), any organic sulphur compound or any phenol which may result in the release of these substances to air	91	9.78
4.2d	any process for the manufacture of a chemical involving the use of any substance mentioned in 4.2(c), if the process may result in a release of that substance to air	415	44.62
4.2e	the manufacture or recovery of carbon disulphide	1	0.11
4.2f	any manufacturing process that may result in the release of carbon disulphide to air	1	0.11
4.2g	the manufacture or recovery of any pyridine or any substituted pyridine	7	0.75
4.2h	the manufacture of any organo-metallic compound	0	0.00
4.2i	the manufacture, purification or recovery of any (designated) acrylate	9	0.97
4.2j	any process for the manufacture of a chemical (which is likely to involve the use in any 12 month period of 1 tonne or more of any designated acrylate or, in aggregate of more than one such designated acrylate	40	4.30
4.3a	any process for the manufacture, recovery, concentration or distillation of sulphuric acid or oleum	22	2.37

Section	Description	Number	Percentage of total
4.3b	any process for the manufacture of any oxide of sulphur but excluding any combustion or incineration process other than the burning of sulphur	6	0.65
4.3c	any process for the manufacture of a chemical which uses, or may result in the release into the air of, any oxide of sulphur (excluding incineration and combustion, other than of S, and releases from the storage and use of SO <sub>2</sub> in cylinders)	20	2.15
4.3d	any process for the manufacture or recovery of nitric acid	3	0.32
4.3e	any process for the manufacture of any acid forming oxide of nitrogen	4	0.43
4.3f	any other process that may result in the release of any acid forming oxide of nitrogen (except from processes covered by Sections 1.1, 2.1 and 2.2)	41	4.41
4.3g	any process for the manufacture (or purification) of phosphoric acid	0	0.00
4.4a	any process for the manufacture of fluorine, chlorine, bromine or iodine or of any other compound comprising only - (i) two or more of those halogens; or (ii) any one or more of those halogens and oxygen	21	2.26
4.4b	any process of manufacture which involves the use of, or which is likely to result in the release into air or into water of any of those 4 halogens or any of the compounds mentioned in 4.4(c) other than the use of any of them as a pesticide in water	51	5.48
4.4c	any process for the manufacture of HF, HCl, HBr and HI or any of their acids	12	1.29
4.4d	any process for the manufacture of chemicals which may result in the release to air of the compounds mentioned in 4.4(c)	61	6.56
4.4e	any process of manufacture (other of chemicals) involving the use of any of four compounds in 4.4(c) (or any of their acids) which may result in the release of these substances into air, other than the coating, plating or surface treatment of metals	12	1.29
4.7a	The manufacture or the formulation of chemical pesticides if the product may result in the release into water of any substance described in Schedule 5 in a quantity which, in any 12 month period, exceeds background by more than the amount stipulated in S5	16	1.72
4.8a	The manufacture or the formulation of pharmaceuticals if the product may result in the release into water of any substance described in Schedule 5 in a quantity which, in any 12 month period, exceeds background by more than the amount stipulated in S5	1	0.11
TOTALS		930	100%

The information in Table 2.1 relates to all processes covered under Sections 4.2, 4.3, 4.4, 4.7 and 4.8 of the Act but not all of these processes are covered by this study. In particular this study concentrates on batch rather than continuous processes. It has been estimated by the Environment Agency that this means that approximately 750 processes are covered by this study, rather than the 930 listed in Table 2.1.

The parts of the chemical industry dealt with in this sector may be broadly characterised by the following points:

1. Table 2.1 shows the large number of processes covered by this study, nearly one third of all IPC authorisations that have been issued, and the significant proportion that fall under relatively broad descriptions. Sections 4.2c and 4.2d, in particular, 'capture' a large number of processes producing a diverse range of chemicals.
2. The use of production campaigns to allow a number of different products to be manufactured with the same equipment.
3. The range of chemicals they produce, for example
  - effect chemicals used in small tonnages in industrial production;
  - intermediates for other chemical producers;
  - speciality chemicals;
  - recovery activities;
  - development chemicals.
4. Typically the client industries for these companies include:
  - other chemical companies;
  - adhesives manufacturers;
  - dyestuffs and pigments manufacturers;
  - users of effect chemicals, including:
    - motor industry;
    - textiles;
    - paper;
    - plastics;
    - surface finishings;
    - agrochemicals.

Companies engaging in these activities range from independent operators with 20 employees and a turnover of £2-3 million to subsidiary operations of blue chip industrial majors. A more detailed assessment of the products and markets is provided in Appendix III.

5. All of the companies are endeavouring to exploit some niche in the market in which they can take advantage of one or more factors such as:
  - specialist technology for which their equipment, patents, or the skills of key personnel offer advantages;
  - rapid and flexible response to customer needs.

Some of the design tasks and control techniques are common to all areas; others are specific to the different steps of the process.

## 2.2 Unit Process Approach

Despite the large number of processes, products and markets covered by this study it is apparent that many processes appear to have the same basic underpinning structure. In particular they have the following stages:

- storage and raw material handling;
- plant systems and equipment;
- reaction;
- separation;
- purification and/or final product preparation.

Whilst there are variations on this theme (usually involving the repeated use of one of more of these units) they are often matters of detail. Thus on the highest level most processes have the same unit sources of releases. The main release points associated with each of these units are summarised below.

Section 5 discusses in more detail the environmental implications of using BAT to prevent and minimise releases from unit processes.

### 2.2.1 Storage and raw material handling

The sector is characterised by the storage and handling of a broad range of raw materials and products, usually in relatively small quantities. The importance of batch operations in the sector means that flexibility in the storage and handling arrangements may be particularly important. The main issues include:

- storage - covers both solids and liquids. The storage of solids will tend to involve dedicated buildings. Liquid storage will involve both bulk and drum storage. The use of drums is particularly prevalent for batch operations;
- handling - batch operations require the use of accurate amounts of reagents. This usually necessitates the use of pre-measuring equipment prior to the reagents being added to the reactor. Handling will also typically involve small quantities.

The main environmental issues associated with storage are the potential for large releases under non-routine conditions and fugitive emissions, respectively. The main issue for raw material handling is fugitive losses.

### 2.2.2 Plant systems and equipment

A wide range of ancillary equipment is required throughout the process. This may include the following systems - ventilation, pressure relief, vacuum raising, pumps, compressors, agitators, valves, purging and heating/cooling. Some of these systems give rise to a waste stream, for example wet vacuum systems, and all of them have the potential to give rise to fugitive emissions.



### 2.2.3 Reaction

Widespread use is made in the sector of reaction vessels constructed from steel or glass-lined carbon steel. Reactors are generally designed to allow the variation of temperature and pressure during the reaction. Reactors usually have a number of inlets/outlets to allow:

- addition of reagents, often in pre-quantified amounts;
- removal of product;
- removal of waste streams, both during (usually volatiles, which may pass to a condenser which returns useful material to the reactor) and after (usually solids and liquids) the reaction;
- addition of an inert reaction atmosphere;
- input of probes that measure reaction conditions;
- emergency venting when reaction conditions deviate from the norm; ...
- maintenance activities.

All of these 'breaks' in the body of reactor are potential release points if not designed and maintained properly. In addition, the reactor will usually have a jacket to allow its temperature to be varied, with either water, steam or some other material being charged to the jacket as temperature requirements dictate.

The main environmental issues associated with the use of a reactor are:

- use of utilities (energy/water etc.);
- control of reaction conditions to maximise yield and minimise waste arisings;
- collection systems for releases of volatiles and particulates; and
- emergency venting systems.

### 2.2.4 Separation

When the reaction is complete, the product(s) need to be separated from the waste(s). This is facilitated by a separation process. A wide range of separation processes are available. These include:

- extraction - which takes advantage of any difference in solubility between the product and waste. A solvent is added to the product/waste mix and preferentially solubilises one of the components. The solvent can then be removed and the product recovered;
- decanting - can be used when the product and the waste are present as immiscible liquids or as solid and liquid;

- filtration - whereby the reaction mix is passed through a filter medium, with the product being allowed through or retained;
- centrifugation - whereby a centrifugal force is applied to the mix to separate out a solid and liquid phase, one of which will contain the product;
- distillation - the reaction mixture is refluxed to fractionally separate the constituent parts;
- crystallisation - crystals are formed and separated from the reaction mixture.

The main environmental issues associated with separation include:

- control over the separation process to maximise recovery;
- the collection and handling of wastes.

### **2.2.5 Purification and/or final product preparation**

Although separation will partition the product from the bulk of the waste streams, it is unlikely to produce the product in the final form. Instead some form of final purification/finishing step is likely to be required. There is a considerable degree of diversity in terms of this step but it may include for example:

- re-application of separation steps;
- drying;
- granulation;
- formulation.

The main environmental issues associated with purification include:

- the control of the purification process to maximise yields;
- the collection and handling of wastes.

Although the unit process approach provides a good high level summary of the processes utilised in the sector, its use should be treated with caution. Each specific chemical process and each specific site will have its own characteristics that preclude a uniform application of BAT. Instead the unit process approach should be seen as a starting point in the identification of BATNEEC, a means of avoiding repetition and ensuring that the Agency's resources are concentrated on the key issues.

In recognition that the unit process approach is insufficiently sensitive to deal with the complexity of the sector, Section 2.3 below provides a summary of the main environmental issues associated with each sub-sector.

## 2.3 Sector specific considerations

This section summarises the main sources of releases and pollutants emitted that are associated with each of the following sub-sectors of the chemical industry (the sub-sectors covered by this report have been broken down in this manner to match earlier Agency reports and guidance):

- organo-metallics (HMSO 1993a, HMIP 1992a);
- sulphonation and nitration (HMSO 1993b, HMIP 1991, HMIP 1992b, HMIP 1993a, HMIP 1995a);
- halogenation (HMSO 1993c, HMIP 1995);
- pesticides (HMSO 1993d, HMIP 1993b);
- pharmaceuticals (HMSO 1993e, HMIP 1993c).

It should be noted that these headings are not mutually exclusive and that, for example, a pharmaceutical process may involve sulphonation etc. In addition, earlier guidance (HMSO 1993f) and research (HMIP 1994a) applies to all of these sectors.

Much of the technical discussion provided in these reports still holds true and it is not the purpose of this study to repeat what has already been done. Instead the study concentrates on highlighting areas where these five types of process may differ from the basic unit process approach outlined in Section 2.2. Annex II to this study develops these sector specific issues in more detail.

### 2.3.1 Organo-metallics

Organo-metallics contain a direct carbon-metal bond. A wide range of metals can form such bonds but the manufacture of organo-metallic compounds is based primarily on just three metals - lead, lithium and magnesium. A number of other organo-metallic compounds are produced on an industrial scale but these are not covered by the IPC system because:

- the only releases from the production of organo-silicons are of hydrogen chloride and therefore these compounds have been covered under hydrogen chloride processes;
- titanium, mercury and cadmium compounds manufactured in the UK contain a metal-oxygen bond and are therefore not truly organo-metallics;
- aluminium compounds are not manufactured in the UK; and
- a wide variety of other compounds (e.g based on gallium, indium and tellurium) are not produced in large enough quantities to warrant control under IPC.

Lead is used in the manufacture of lead alkyls which, despite the rapidly increased market share of lead-free fuel, is still used as an anti-knock agent in petrol. The main lithium based product, n-butyllithium, is used as an initiator for polymerisation processes, whilst magnesium is used to produce Grignard re-agents, important precursors in a wide range of chemical syntheses.

Whilst each of these three types of compound require unique approaches towards their production, there are also a number of issues common to them all. These include:

- strongly exothermic reactions, which if they go wrong can result in the need to vent the contents of reactors;
- the sensitivity of the reactions to the presence of atmospheric oxygen and moisture, which can compromise product quality and in certain cases can give rise to pyrophoric reactions;
- the use of large amounts of hydrocarbon based solvents to avoid moisture problems;
- the presence of both organic and metal based pollutants in wastestreams;
- the use of large stoichiometric excesses improves yields but increases raw material use and waste arisings;
- a large number of side reactions that can reduce reaction yields and increase the complexity of the waste produced.

In addition to these general issues, the production of each type of compound gives rise to a number of specific issues. These include:

### **Lead compounds**

Although there is still a market for lead alkyl products, particularly outside Western Europe and North America, the generally declining requirements for these products means that there is limited research and development into innovation in process or pollution control techniques.

All existing processes are based on the batch wise reaction of lead/sodium alloy with ethyl or methyl chloride. The main issues to note with this type of reaction are:

- tetramethyllead (TML), but not tetraethyllead (TEL), is unstable on its own and is thus manufactured, stored and sold as an 80:20 mixture with toluene (utilised because of its similar vapour pressure to TML);
- a large excess of lead needs to be used during the process, with the result that up to 75% of the lead in the reaction is not incorporated into the product and so needs to be recovered from the process. Other reagents, alkyl chlorides etc., are also used in excess and need to be recovered;
- the reaction usually takes place under pressure to ensure that the normally gaseous alkyl chloride reagent is present in the reaction vessel as a liquid;
- TEL can be removed from gas streams by use of mineral oil based, packed tower absorbers. TEL is recovered from the oil by stripping under vacuum with heating. Incineration can also be used;

- waste waters will typically receive pH adjustment followed by settlement to remove inorganic lead compounds. Lead rich sludges can be collected and sent for recovery. Soluble organo-lead compounds can be removed by reduction with sodium borohydride or zinc. Alternatively chemical precipitation followed by adsorption and ozone can be used.

The key process units and sources of emission involved in the reaction are summarised in Table 2.2.

**Table 2.2 Key process units and sources of emission associated with the manufacture of organo-lead compounds**

Process unit	Activity	Main emission
Reactor (commonly known as an autoclave)	<ul style="list-style-type: none"> <li>• Reagents are charged to reactor with catalyst where they are refluxed at the desired pressure and temperature (typically 6 bar for TEL and 24 bar for TML and approx. 65 °C for both, respectively).</li> </ul>	<ul style="list-style-type: none"> <li>• Hydrocarbons and alkyl chloride (methane, butane) vented from reflux;</li> <li>• Excess alkyl chloride vented off at completion of reaction.</li> </ul>
Batch still (reactor)	<ul style="list-style-type: none"> <li>• Reaction mass from autoclave is transferred to a batch still pre-charged with water. TML/TEL then distilled off by direct steam injection and condensed and collected in a separation vessel.</li> </ul>	<ul style="list-style-type: none"> <li>• Remaining alkyl chloride driven off as batch still heated;</li> <li>• Still residues (primarily lead, sodium chloride, sodium hydroxide and alkyl chloride).</li> </ul>
Phase separation	<ul style="list-style-type: none"> <li>• Remaining water and impurities removed from TML/TEL by phase separation.</li> </ul>	<ul style="list-style-type: none"> <li>• Lead and other impurities in aqueous stream.</li> </ul>
Blending	<ul style="list-style-type: none"> <li>• TML/TEL blended with a variety of material to form final product.</li> </ul>	<ul style="list-style-type: none"> <li>• Dibromo- and dichloro- ethane from blending process.</li> </ul>
Collection pits	<ul style="list-style-type: none"> <li>• Effluents from the various stages in the process are directed to collection pits for the recovery of lead.</li> </ul>	<ul style="list-style-type: none"> <li>• TEL/MEL vapours.</li> </ul>

### Lithium alkyls

By far the most important lithium alkyl is n-butyllithium, which is used extensively as an initiator in polymerisation reactions. All commercial production of n-butyllithium is based on the reaction of lithium metal with n-butyl chloride.

The most important elements of the production of n-butyl lithium are:

- some reagents and the product are pyrophoric and they also react exothermically with water to form butane gas. The process therefore takes place in a hydrocarbon solvent which excludes moisture and air. The main solvents used are pentane, hexane and cyclohexane;

- large amounts of inert gas (nitrogen and argon) are used during parts of the process and these will entrain volatiles;
- vents are fitted with oil bubblers to prevent the ingress of air/moisture into the process. Oil from these bubblers may be volatilised and lost to atmosphere;
- lithium metal is expensive and therefore considerable attention is paid to its recovery during the process.

The main process steps, emission points and substances released are outlined in Table 2.3.

**Table 2.3 Key process units and sources of emission associated with the manufacture of organo-lithium compounds**

Process unit	Activity	Main emission
Reactor	<ul style="list-style-type: none"> <li>• Lithium ingots melted in mineral oil at 180-190 °C and then cooled to form 'clean' finely divided lithium. The mineral oil is drained from the reactor and a hydrocarbon solvent added to wash the lithium. This too is drained from the reactor to form a lithium dispersion.</li> </ul>	<ul style="list-style-type: none"> <li>• Mineral oil drained from the reactor and hydrocarbon wash contaminated with lithium;</li> <li>• Hydrocarbon solvent emissions to air.</li> </ul>
Reactor	<ul style="list-style-type: none"> <li>• Lithium dispersion charged to reactor and butyl chloride added at a constant rate.</li> </ul>	<ul style="list-style-type: none"> <li>• Hydrogen;</li> <li>• Hydrocarbon solvent emissions.</li> </ul>
Filtration	<ul style="list-style-type: none"> <li>• Reaction mass is filtered twice. The resulting filtrate is the product.</li> </ul>	<ul style="list-style-type: none"> <li>• Filter cake sent for recovery.</li> </ul>

### Organo-magnesium

Organo-magnesium compounds are used extensively as Grignard reagents. A wide variety of reactions have been developed to produce specific compounds but typically these can be viewed as the displacement of a halogen by magnesium from the desired organic group. A key issue in the production of organo-magnesium compounds is that:

- they are always made and used in an organic solvent, typically ethers (e.g tetrahydrofuran) which provide good solubility.

Given the wide variety of reactions that can be used to form Grignard reagents it is difficult to generalise about the process steps involved but a typical reaction may consist of the steps, emissions and substances outlined in Table 2.4.

**Table 2.4 Key process units and sources of emission associated with the manufacture of organo-magnesium compounds**

Process unit	Activity	Main emission
Reactor	<ul style="list-style-type: none"> <li>Solvent and magnesium metal charged to reactor before the controlled addition of an organo-halide.</li> </ul>	<ul style="list-style-type: none"> <li>Alkyl halide and solvent emissions to air.</li> </ul>
Reactor	<ul style="list-style-type: none"> <li>Reaction mass transferred to another reactor for the addition of a second organic compound.</li> </ul>	<ul style="list-style-type: none"> <li>Solvent emissions to air.</li> </ul>
Distillation	<ul style="list-style-type: none"> <li>To recover solvent.</li> </ul>	<ul style="list-style-type: none"> <li>Solvent emissions to air;</li> <li>Distillation column 'bottoms'.</li> </ul>
Phase separation	<ul style="list-style-type: none"> <li>Reaction mass is acidified with the result that magnesium salts are driven into aqueous phase. Product concentrates in organic phase.</li> </ul>	<ul style="list-style-type: none"> <li>Aqueous phase for effluent treatment.</li> </ul>

### 2.3.2 Sulphonation and Nitration

Sulphonation and nitration reactions are traditionally considered in terms of the following reactions:

- sulphonation and nitration of aromatics;
- aliphatic sulphonation/sulphation;
- explosives nitrations.

A wide range of sulphonating/nitrating agents are available and the particular agent selected and reaction undertaken may give rise to particular environmental problems. In addition, there are a number of issues that are likely to arise whichever combination of agent/reaction is used. These are:

- the diversity of raw materials and products;
- the use of large excesses of acid to drive the reaction. The excess acid can be recovered and returned to the process;
- nitration will lead to the formation of NO<sub>x</sub> rich gases. These are diluted with air to change the NO<sub>x</sub> into NO<sub>2</sub> and this can be treated in a scrubber containing weak caustic soda;
- sulphonation often generates a SO<sub>3</sub> rich gas stream which can be treated in a ceramic packed scrubber containing 98% sulphuric acid, followed by a candle filter to eliminate mist;

- cyclones are often used to remove surplus liquid. The off gases from the cyclone can be passed to an electrostatic precipitator.

Each of these reactions and the main emissions associated with them are summarised in the Tables below:

**Table 2.5 Key process units and sources of emission associated with aromatic sulphonation and nitration**

Process unit	Activity	Main emission
Reactor	<ul style="list-style-type: none"> <li>• Organic material plus sulphonating/nitrating agent (usually sulphuric acid for the former, or a mixture of sulphuric acid/nitric acid, commonly known as mixed acid, for the latter) charged to reactor. A wide range of operating conditions may be used but typically atmospheric pressure and 100°C;</li> <li>• On completion of the reaction, the mixture is quenched in water or an ice slurry (this may take place in a separate vessel).</li> </ul>	<ul style="list-style-type: none"> <li>• Acid vapours (largely sulphuric or nitric acid) from the reaction and quenching;</li> <li>• Unreacted sulphonating/nitrating agent arising from the use of an excess to drive the reaction;</li> <li>• Solvent emissions.</li> </ul>
Separation	<ul style="list-style-type: none"> <li>• Quenched mixture is separated using pressure filtration.</li> </ul>	<ul style="list-style-type: none"> <li>• Filtrate contaminated with unreacted raw material and acid. Some may be recycled, most is neutralised with lime to form gypsum;</li> <li>• The product is washed on the filter and the resulting dilute acidic wash waters neutralised.</li> </ul>

**Table 2.6 Key process units and sources of emission associated with sulphonation and sulphation of aliphatics**

Process unit	Activity	Main emission
Reactor	<ul style="list-style-type: none"> <li>• Sulphur trioxide is often used as the sulphonation/sulphation agent and reacted with an aliphatic organic compound.</li> </ul>	<ul style="list-style-type: none"> <li>• Acidic vapours from the reaction and the sulphur trioxide production process;</li> <li>• VOC emissions.</li> </ul>
Neutralisation	<ul style="list-style-type: none"> <li>• The acid reaction product is neutralised and sent for storage.</li> </ul>	<ul style="list-style-type: none"> <li>• Vapours from the neutralisation.</li> </ul>



**Table 2.7 Key process units and sources of emission associated with Explosives Nitrations**

Process unit	Activity	Main emission
Reactor	<ul style="list-style-type: none"> <li>Glycerine or cellulose is nitrated with mixed acid;</li> <li>Resulting reaction mixture is chilled.</li> </ul>	<ul style="list-style-type: none"> <li>Nitrogen oxide off gases.</li> </ul>
Separation	<ul style="list-style-type: none"> <li>The chilled emulsion is separated and washed with water;</li> <li>Spent acid from separation is distilled to obtain the nitric and sulphuric components.</li> </ul>	<ul style="list-style-type: none"> <li>Nitric acid and sulphuric acid from distillation.</li> </ul>

### 2.3.3 Halogenation

Halogenation is characterised by a very wide variety of reaction options, although a number of environmental issues are associated with virtually all options. These include:

- the potential for release of organo-halogens;
- the potential for the formation of dioxins;
- sophisticated storage and handling techniques may be required.

The main process units and emissions associated with halogenation processes are summarised in Table 2.8 below.

**Table 2.8 Key process units and sources of emission associate with Halogenation**

Process unit	Activity	Main emission
Reactor	<ul style="list-style-type: none"> <li>Organic feed is reacted with halogenating agent.</li> </ul>	<ul style="list-style-type: none"> <li>VOCs (potentially organo-chlorines);</li> <li>Halides and halogens.</li> </ul>
Separation	<ul style="list-style-type: none"> <li>A wide variety of techniques may be applied.</li> </ul>	<ul style="list-style-type: none"> <li>Washwaters from filtration and VOCs from evaporation.</li> </ul>

A wide range of halogenating agents are available and some of the advantages and disadvantages of their use are summarised in Table 2.9 below.

**Table 2.9 Main halogenating agents**

Halogenating agent	Advantage	Disadvantage
Chlorine	<ul style="list-style-type: none"><li>• Many reactions will generate only gaseous by-product streams, which are easily removed from the off gas;</li><li>• On completion of the reaction only small amounts of chlorine usually remain.</li></ul>	<ul style="list-style-type: none"><li>• Sophisticated storage and handling facilities are normally required.</li></ul>
Bromine	<ul style="list-style-type: none"><li>• As for chlorine;</li><li>• Can be contained in small, easily handled containers.</li></ul>	<ul style="list-style-type: none"><li>• As for chlorine.</li></ul>
Iodine	<ul style="list-style-type: none"><li>• Readily available;</li><li>• Does not require sophisticated storage facilities.</li></ul>	<ul style="list-style-type: none"><li>• Charging of solids to the reaction vessel may require special solids handling equipment;</li><li>• Difficulties with certain waste disposal routes.</li></ul>
Thionyl chloride/ Sulphuryl chloride	<ul style="list-style-type: none"><li>• Many reactions will generate gaseous by-product streams which are most easily removed from the off gas;</li><li>• Readily available in containers up to 200 litres;</li><li>• Does not require sophisticated storage facilities.</li></ul>	<ul style="list-style-type: none"><li>• Reacts violently with water, alcohols etc.;</li><li>• On completion of the reaction considerable excess quantities can remain and these have to be removed by distillation;</li><li>• Removing the reaction product may be difficult.</li></ul>
Phosphorus tri and penta chloride	<ul style="list-style-type: none"><li>• Readily available in containers up to 150 litres and in bulk;</li><li>• On completion of the reaction may be removed by filtration.</li></ul>	<ul style="list-style-type: none"><li>• Charging of the solids to the reaction vessel may require special solids handling equipment;</li><li>• Effluent containing phosphorus compounds may require specialist treatment;</li><li>• Reacts violently with water and fumes on contact with moist air.</li></ul>
Aluminium chloride	<ul style="list-style-type: none"><li>• Readily available;</li><li>• Does not require sophisticated storage facilities;</li><li>• Can be used to carry out chemical reactions to produce substances which would be difficult to make using other approaches.</li></ul>	<ul style="list-style-type: none"><li>• Fumes readily in contact with moist air generating hydrogen chloride and aluminium hydroxide;</li><li>• Generates a considerable volume of aqueous effluent containing aluminium salts. This effluent is usually highly acidic;</li><li>• Charging of solids to the reaction vessel may require special solids handling.</li></ul>
Hydrogen halides	<ul style="list-style-type: none"><li>• Readily available in anhydrous form or aqueous solution;</li><li>• May generate no gaseous by-product.</li></ul>	<ul style="list-style-type: none"><li>• Sophisticated storage and handling facilities are often required.</li></ul>

### 2.3.4 Pesticides

The manufacture of pesticides utilises the basic unit processes outlined in Section 2.2 but raises a number of particular environmental issues, including the:

- interaction of environmental and workplace health/safety regulatory systems with the pesticide approval system;
- storage, handling and use of particularly hazardous substances;
- disposal of hazardous wastes;
- use of high integrity packaging and materials handling equipment;
- need for frequent washdown between batches;
- production of pesticides usually consists of two stages:
  - a primary production step in which the active ingredient is manufactured;
  - a secondary formulation step whereby the active ingredient is combined with inert materials to form the final product.
- the generation of dusts that may contain active ingredients. HEPA filtration may be required to abate such gas streams.

The main emissions to the environment associated with the primary and secondary manufacture of pesticides are summarised in Tables 2.10 and 2.11, respectively.

**Table 2.10 Key process units and sources of emission associated with the primary manufacture of pesticides**

Process unit	Activity	Main emission
Reactor	<ul style="list-style-type: none"><li>• Raw materials are reacted in a solvent.</li></ul>	<ul style="list-style-type: none"><li>• Dusts from vessel charging with dry raw materials;</li><li>• Aqueous effluents;</li><li>• VOCs due to solvent use etc.;</li><li>• Washdown effluent.</li></ul>
Separation	<ul style="list-style-type: none"><li>• A wide variety of separation techniques may be used.</li></ul>	<ul style="list-style-type: none"><li>• Distillation column 'bottoms';</li><li>• VOCs from distillation columns.</li></ul>

**Table 2.11 Key process units and sources of emission associated with the secondary manufacture (formulation) of pesticides**

Process unit	Activity	Main emission
Crusher and/or pulverizer	<ul style="list-style-type: none"> <li>Raw materials are crushed or pulverised to get them into the correct physical form for reaction.</li> </ul>	<ul style="list-style-type: none"> <li>Dusts from vessel charging with dry raw materials;</li> <li>Dusts from crushing/ pulverizer.</li> </ul>
Blending	<ul style="list-style-type: none"> <li>The active ingredient may be blended with a number of other materials to produce the final product.</li> </ul>	<ul style="list-style-type: none"> <li>Dusts and VOCs from blending.</li> </ul>
Milling	<ul style="list-style-type: none"> <li>The final product may require milling to ensure that it is in the correct physical form.</li> </ul>	<ul style="list-style-type: none"> <li>Dusts from milling.</li> </ul>
Packaging	<ul style="list-style-type: none"> <li>High standards of packaging will be required to ensure that the product is not inadvertently released as well as to preserve product quality.</li> </ul>	<ul style="list-style-type: none"> <li>Dusts from moving dry materials down chutes etc.</li> </ul>

### 2.3.5 Pharmaceuticals

The manufacture of pharmaceuticals utilises the basic unit processes outlined in Section 2.2 but raises a number of particular environmental issues, including the:

- interaction of environmental and workplace health/safety regulatory systems with the pharmaceutical approval system. This interaction can make proposed changes to the process time consuming and costly to implement;
- importance of preventing cross contamination between product and environment. Modern processes will tend to be designed on the basis of containment (e.g collection and treatment of workplace air as well as process gas streams) and island systems (i.e separation of process units from each other and from support services);
- storage, handling and use of particularly hazardous substances;
- long timescales involved with developing products;
- use of certain production techniques that are unlikely to be applied in other parts of the chemical industry e.g natural separation and fermentation;
- formulation of the product into a form (tablet, capsule, ointment) that is unlikely to be used elsewhere in the chemical industry;
- high levels of cleanliness and product quality required;

- limitations on the opportunity to recycle, particularly VOCs, because of raw material and product quality requirements;
- the generation of dusts that may contain active ingredients. Such streams may require the use of HEPA filtration.

The main emissions to the environment associated with the primary and secondary manufacture of pharmaceuticals are summarised in Tables 2.12 and 2.13, respectively.

**Table 2.12 Key process units and sources of emission associated with the primary manufacture of pharmaceuticals**

Process unit	Activity	Main emission
Reactor	<ul style="list-style-type: none"> <li>• Raw materials are reacted in a solvent.</li> </ul>	<ul style="list-style-type: none"> <li>• Dusts from vessel charging with dry raw materials;</li> <li>• Washdown effluent.</li> </ul>
Separation	<ul style="list-style-type: none"> <li>• The active ingredient is separated from by-products and waste.</li> </ul>	<ul style="list-style-type: none"> <li>• VOCs;</li> <li>• Separation wastes.</li> </ul>
Natural extraction	<ul style="list-style-type: none"> <li>• This is an alternative to use of a reactor;</li> <li>• It involves repeated extraction of the active ingredient from natural materials.</li> </ul>	<ul style="list-style-type: none"> <li>• Large amounts of waste from the natural material.</li> </ul>
Fermentation	<ul style="list-style-type: none"> <li>• Fermentation involves the inoculation of micro-organisms in a liquid broth in the presence of nutrients.</li> </ul>	<ul style="list-style-type: none"> <li>• waste liquid broth from centrifuging etc.;</li> <li>• solvents, filter residues and wash materials from product recovery.</li> </ul>
Drying	<ul style="list-style-type: none"> <li>• May be used to remove excess solvent.</li> </ul>	<ul style="list-style-type: none"> <li>• VOC emissions to air.</li> </ul>

**Table 2.13 Key process units and sources of emission associated with the secondary manufacture of pharmaceuticals**

Process unit	Activity	Main release
Sieving/milling/microionizing	<ul style="list-style-type: none"> <li>• May be required to ensure that no foreign matter is present and that the raw materials/active ingredients are present in the correct physical form.</li> </ul>	Particulates.
Weighing	<ul style="list-style-type: none"> <li>• Very accurate weighing procedures may be needed;</li> <li>• Cleaning of weighing equipment between batches will be required.</li> </ul>	Particulates.

Process unit	Activity	Main release
Mixing/blending	<ul style="list-style-type: none"> <li>• May need to add fillers (sugar or starch) etc. to the active ingredient and ensure that they are well mixed;</li> <li>• Wet or dry blending may be used.</li> </ul>	Particulates.
Granulation	<ul style="list-style-type: none"> <li>• This ensures that the active ingredient is present in the correct physical form prior to encapsulation, tablet forming etc.</li> </ul>	Particulates (dry process); Solvent (wet process).
Drying	<ul style="list-style-type: none"> <li>• Drying is often required to remove any excess solvent;</li> <li>• Tray ovens, fluidized beds, vacuum driers, tumble driers, spray driers and freeze driers may be used;</li> <li>• Solvent concentrations within the drier must be carefully controlled to avoid potential explosion problems. This often requires dilution with air which may make more abatement difficult.</li> </ul>	VOCs.
Tablet pressing, printing and coating	<ul style="list-style-type: none"> <li>• After blending the active ingredient with a binder and/or lubricant it is pressed into a tablet;</li> <li>• Collection of tablets in containers may result in dust problems;</li> <li>• Printing is used to apply a brand or manufacturer's name. The ink is usually butanol/ethanol based;</li> <li>• Coating imparts physical strength to the tablet. Water based coatings are increasingly replacing solvent based ones. Exceptions may be where water insoluble (slow release) tablets are being produced.</li> </ul>	Particulates.
Filling and packing	<ul style="list-style-type: none"> <li>• High standards of packaging will be required to ensure that the product is not inadvertently released as well as to preserve product quality.</li> </ul>	Dusts from moving dry materials down chutes etc.
Aerosol preparation	<ul style="list-style-type: none"> <li>• Aerosols are filled, capped, tested and weighed in specialist equipment.</li> </ul>	Leaks of propellants.

### 3. TECHNIQUE EVALUATION

This section outlines the approach that has been taken during the study to evaluate techniques for their suitability for preventing, minimising or rendering harmless releases from processes in the sector.

It also briefly outlines the approach that has been adopted to characterise techniques. Subsequent sections critically appraise the utility of these techniques in the sector, whilst Appendix A provides a concise summary of all techniques discussed in this report.

#### 3.1 How to determine BATNEEC

Whilst technical definitions exist for each of the words comprising the phrase best available techniques not entailing excessive cost (BATNEEC) these definitions are difficult to apply in practice. The overall problem can be considered in two parts:

1. What are the potential best available techniques (BATs)?
2. Which of these does not entail excessive cost (NEEC)?

The major problem with BAT is how to decide which of a variety of techniques is "best" i.e. the **most effective** at preventing, minimising or rendering harmless releases, this is the definition of best used in the guidance to the regulations. A whole raft of factors will affect the judgement as to which technique is "best" in the particular circumstances of a given process.

The main physical factors will usually be the chemicals involved, their physical form and properties and the precise conditions of the release, including its magnitude and frequency. There are also likely to be other factors associated with some techniques such as how well they fit within the current organisational framework and philosophy of the site and the company concerned.

The major problems relating to NEEC tend to relate to site position, the timetable for improvements and "sector affordability", although the nature and magnitude of the release may also play a part in the decision, as may the age of the process. For example, it may be BAT to have some kind of emission control device on the breather vent of a liquid storage tanks but this may well be EEC (i.e. not NEEC, and excessive) if the liquid being stored has low volatility, low toxicity, a high odour threshold and the process is far away from human habitation. A more detailed assessment of NEEC considerations as they apply in this sector is provided in Appendix C.

The dependence of the BATNEEC decision on process, chemical and site specific considerations and the wide variety of processes involved make it virtually impossible to be prescriptive in a general way about BATNEEC for the sector. The specific conditions associated with the process have to be taken into account in the decision making. In the absence of prescriptive guidance it seems best to classify the issues that should be considered in each specific case in order to reach a conclusion on BATNEEC for the process of concern.

The following Table is presented as a list of the issues involved to help decision making by Inspectors in particular cases. It is proposed that this list should form the basis for Inspectors to reach a judgement on whether a particular process operator has taken account of all the relevant issues in deciding what constitutes BATNEEC for the authorisation in question. It could also be used by authorisation applicants in considering their application.

The detailed compendium of techniques given in Appendix A to this report could be used to further probe the proposal by providing a range of techniques that could be alternatives to the ones selected. Any rigorous assessment of BATNEEC by the process operator would be expected to have considered these alternatives and have a reasoned argument as to why they were less suitable than the option selected and presented in the authorisation application. It would clearly help the Inspector in dealing with the application if it contained some of the information about alternative techniques and the reasons for the selected preference.

### **3.2 What factors are involved in BATNEEC decisions?**

In order to help BATNEEC decisions it is helpful to consider each of the following relevant factors. Table 3.1 below lists the factors that are likely to be involved and identifies the major issues associated with each factor and some suggestions on the approach that might be used to help make a decision. Each factor has been assigned to one of the following groups:

- an availability factor designated by **a**;
- a “best” i.e. most effective factor designated by **b**;
- a cost factor designated by **c** (more extensive guidance is provided in Appendix A);
- an excessive factor i.e. the amount by which the net costs of the technique exceed the environmental benefit resulting from its application designated by **e**.

### **3.3 Characterisation of techniques**

For the purposes of this study it has been decided to discuss techniques for the prevention and minimisation of releases under the following broad headings:

- management techniques;
- process techniques;
- abatement techniques, including:
  - air techniques;
  - waste water techniques;
  - land techniques.



**Table 3.1 Factors involved in the identification of BATNEEC for the sector**

Factor	Issues to consider	Approach
a Availability of the technique	Number of suppliers, their location and any special requirements for consumables e.g. catalysts or other operating requirements that may limit its use.	Use personal experience, suppliers information and the authorisation register
b Overall environmental performance	Techniques will often have an environmental impact of their own. How does this impact compare with the impact that the technique was originally intended to mitigate?	Consider an inventory of inputs and outputs, pay particular attention to intermedia transfers which may warrant a consideration of BPEO
b Technique effectiveness and support needs	Achievable release limits from the technique. Performance of technique in avoiding, minimising and finally abating substance releases.	Use manufacturer's information and practical experience from other similar processes. Other sources of information are ETBPP and the register of IPC authorisations. Ensure that any pilot studies are an accurate representation of actual operating conditions
b Operational reliability	Frequency of maintenance and any changes in performance over working life of technique. What checks need to be made on performance? What happens during maintenance and start-up? Can dual systems be used to provide suitable cover or back up?	Use manufacturer's information, practical experience and monitoring information from other authorised processes
b Track record	Is the technique well tried and tested or novel and not fully tested in the field?	Consider other examples of use of techniques. Does the process operator have the experience to operate the technique?
b Operating range	Matching the operating characteristics of the technique with the substances and their amount, flow rate and frequency of release. Intermittent releases can require different techniques from those for continuous ones.	Compare expected release pattern with technical specification of technique. Particular attention needs to be paid in this sector to the diversity of products that may be produced by a batch based process. Can the technique deal with this diversity? Consideration also needs to be given to performance during start up and shut down, which will constitute a significant proportion of operating time in this sector.
b Raw material use	Material required to operate the technique e.g. filter media in filters. What techniques are proposed for dealing with these wastes?	Consider input output inventory and if required consider BPEO analysis
b Energy use	Energy needed to keep technique running and any special start up or shut down requirements.	Use manufacturer's specifications and any track record

Factor	Issues to consider	Approach
b Health and safety implications	Consider normal operating conditions and maintenance implications, look for toxic material use and other hazards. What plans are in place to deal with them?	Consider operating conditions and any special features associated with non-routine activities such as maintenance and breakdown.
b Technical support	Robustness of technique. Will the manufacturer continue to provide specialist technical support.	Consider degree of automation, continuous technique monitoring and control particularly for key control parameters
b Maintenance implications	What happens to the releases during maintenance and other shut down periods.	Use of back-up systems may be necessary.
b Noise, vibration and visual implications	These broader issues will become part of the considerations under IPPC and may be relevant under IPC for particular locations.	Use experience from other sites, visual aspects should be clear from design and location information.
c Operational lifetime	A factor to be considered with the installation and capital cost.	Use manufacturer's information and track record.
c Installation requirements	There are likely to be differences between new and existing processes. In some cases retrofitting techniques may be impossible because of size and space constraints.	Consider site plans and information on technique requirements.
c Capital costs	Capital costs may include more than just technique i.e integrating it with wider process/site.	Use manufacturer's information and track record.
c Running costs	Materials and utilities used and time taken in maintenance.	Use manufacturer's information and track record.
c Cost savings	Value of material recovered and avoided waste management costs. Also consider whether separation and collection earlier in the process would increase recovery and recycling potential.	Use average costs of materials and an average day rate for estimating cost savings.
e Reduction in environmental impact	The areas likely to be impacted by releases from the process and their sensitivity to damage, the properties of the substances released and their quantities and release profile over time. It is also necessary to take account of existing levels of pollution in the areas likely to be impacted.	Use information on reduction in overall release of priority chemicals and at a more detailed level use the methodology proposed for BPEO assessment.

## **4. MANAGEMENT TECHNIQUES**

### **4.1 Introduction**

This section is concerned with the way that processes are designed, managed and operated so as to achieve the IPC objectives of preventing, minimising and rendering harmless any releases. It is, however, hard to draw a boundary between those management techniques that are key to achieving these objectives and those that are simply "good management" in the broadest sense. This section will not seek to be too fastidious in this distinction. Indeed experience suggests that organisations that are generally "well managed" are usually effective in achieving all their objectives whether these are reduced environmental impact, improved safety or increased profitability. The converse often also applies.

A key issue therefore from the point of view of the IPC objectives is how the company owning the process actually views its environmental impact. The first part of this section will present a brief synopsis of corporate environmental positioning as it relates, in particular, to the chemical industry. The next part will consider the key issue of staff awareness and engagement since it is certainly possible for companies to present a high level environmentally responsible image but fail to commit to it and thence to deliver. The final section will consider the "techniques" themselves. Management techniques appropriate to the sector are summarised in Appendix A.

There can be no doubt that the most effective and efficient way of implementing pollution prevention is to integrate these aspirations and objectives into the management and operation of the company. There are many techniques that are deployed to achieve these overall objectives and it is difficult to say that one is better than another. The precise actions and routes companies follow in making decisions will vary and no one route will necessarily be right under all circumstances. The technique that is "best" has to fit the style and culture of the organisation concerned. It follows that what is "best" for one process may not be "best" for another. The main role of Inspectors is to satisfy themselves that the techniques selected are adequate to ensure that the environmental impacts of process operation are identified and adequately controlled.

### **4.2 Corporate environmental positioning**

There is a great deal of literature concerned with the way that companies and organisations adopt and implement their environmental responsibilities to different degrees. The intention here is not to enter this field in depth but merely to present some of the relevant points to emerge from these analyses. This is intended to assist Inspectors in identifying the motivation that different company managements may be deploying in relation to particular process operations. The general picture is that many companies within this sector are attempting to position themselves as being highly environmentally responsible, but it is the real, demonstrable improvement in environmental performance that matters to the Agency.

#### 4.2.1 Companies in general

There have been many attempts to categorise and characterise the responses of different companies to environmental pressures. Three examples of specific classification exercises applied to companies in general are summarised in Table 4.1. This Table shows the titles of the different characteristic responses to environmental issues taken by companies and identified by the authors. The titles are fairly self-explanatory and, for our purposes, they convey sufficient information, if required more details can be found in the references.

**Table 4.1 Examples of environmental positioning of companies**

Author		
Dodge (1997)	Azzone (1997)	Hart (1997)
Resistance	Passive, lobbying based	
Observe and comply	Reactive	
Accommodate		Pollution prevention
Seize and pre-empt	Anticipatory "green"	Product stewardship
Transcend	Innovative "green"	Clean Technology

In practice it is likely that most companies will at one stage or another adopt more than one type of response to deal with specific issues. It is therefore the overall approach adopted that is of relevance. It is interesting that all of the bottom three rows in this Table imply company responses that go far beyond simple compliance with current regulations and seek to move to utilise minimal environmental impact as a positive force for market success. It is clearly in the Agency's interest to encourage companies to move into these positions. Many chemical companies are among the world leaders in aspiring to be in the highest environmental categories of transcending environmental regulations and introducing innovative green and clean technologies.

#### 4.2.2 UK Chemical Industry

While the general picture in the UK is not quite as rosy as indicated above, a few UK based companies are in the "world leader" category and the chemical sector is on the whole among the most environmentally aware. A survey by the Environmental Technology Best Practice Programme of environmental awareness in eleven industrial sectors is summarised in Table 4.2. One of the sectors covered was the fine and speciality organic chemical sector with 99 companies surveyed.

**Table 4.2 Results of survey of companies in chemical sector**

Issue	Percentage responded "yes"	Comment
Environmental issues affect our profitability	29	All other sectors had a lower response - between 0% and 10%
There is no significant benefit to us from improving our environmental performance	18	The lowest response from all the sectors
We are considering or have a corporate environmental policy	95	The highest response of any sector - 80% already have a policy.
Respondents felt they were not well informed about options and technology to meet environmental regulations	10	The second lowest response i.e. they felt well informed
It would be easier to comply if better advice were available	28	The lowest by a long way the next lowest sector had a 64% response
Aware of ETBPP	45	
What is the most important perceived benefit from improved environmental performance		
better customer image	35	
better image in local community	46	
cost reduction	33	
safer working environment	17	
no benefit	4	
What was the actual most important benefit from improved environmental performance		
better image among employees	18	
increased efficiency	30	
waste reduction	28	
saved money	31	
complied with legislation	34	

The results indicate that the chemical sector was the most environmentally aware of all the sectors surveyed. This was interpreted, in the report, as being due to the attention given to the sector by both pressure groups and regulators. As a result of this high profile the environment is considered a business issue within this sector unlike several of the others. This sector also shows the highest perceived and actual appreciation of the returns in cost savings and efficiency that result from improved environmental performance.

Another example that supports the contention that the sector as a whole is taking its environmental responsibilities seriously is that of "Responsible Care" (CIA 1989). "Responsible Care" is a world wide initiative and introduced in the UK in 1989 in an attempt to counter the

adverse publicity it was receiving in relation to its perceived environmental impact and its response to that perception.

The latest report from the Chemical Industry Association (CIA) on industry performance in the UK shows a number of achievements such as reductions in "red list" substance releases from 360 tonnes in 1990 to 37 tonnes in 1996 and a 10% reduction in energy use over the same period. The report also indicates that 64% of CIA member sites produce reports on the environmental impacts of their activity and 89% of sites have formal complaint procedures.

However, while progress is being made in reducing loads and impacts, and additional steps such as the formation of Community Advisory Panels involving local communities in plant operational issues are being taken, there is little sign, so far, of public perceptions changing. For example, Chemical Week reported in the July 2/9, 1997 edition that the "favorability towards the industry among opinion leaders is" only 23% in the US and a similar low level 25%-42% exists across Europe. There is similar evidence from a recent survey by ICEM of workers and trade union representatives from the chemical industry which showed that 35% of respondents were not aware of the Responsible Care programme. Although Unions and workers in North Western Europe were more likely to be aware of and be involved in the initiative.

### **4.3 Management Techniques**

In discussing management techniques it is difficult to draw a line between management techniques that are simply part of good site management and those that are key to pollution prevention and control. A whole raft of items could be collected here as management techniques which could contribute to reductions in releases from and the environmental impact of processes. Many of them would be very process specific such as the scheduling of batch processes to avoid cleaning of reactors. Others would amount to little more than applied common sense, for example, keeping the site tidy. In this section we have attempted to strike a useful balance and in order to introduce some structure have presented the techniques in sections. The sections selected derive from the six root causes of quality problems in companies (Sayle 1988) namely:

1. Lack of organisation.
2. Lack of training.
3. Lack of discipline.
4. Lack of resources.
5. Lack of time.
6. Lack of senior management commitment.

### 4.3.1 Organisation

#### Responsibility

One of the most important aspects of organisation in relation to the achievement of any objective is that there is a clear understanding of where responsibilities lie. In relation to pollution prevention and IPC compliance the same understanding is necessary and there should be a single point contact within an organisation for the authorisation of a given process.

This person should be sufficiently senior in the management hierarchy for his/her points and arguments to be listened to seriously. Consideration of an organisational chart for the site and process, by the Inspector, and relevant job descriptions should enable this to be established if it is not already apparent from previous experience or other information. It would be expected that there is a clear delineation of authority relating to the authorisation between those responsible for the environment on a corporate and a site basis and those that operate the process. This desire for clarity should not, however, result in a culture within the organization that views the single point contact as the sole person responsible for complying with the authorisation. Instead the process operator should be able to demonstrate that all roles and responsibilities necessary to ensure compliance have been identified, assigned and recorded.

Many companies have a site management committee that meets regularly to discuss all issues relating to the site. It may be expected that the environment manager or equivalent is a member of such a committee and that the environment is a regular, minuted agenda item. In some cases companies demonstrate management commitment to health, safety and environment issues by always having this item first on the meeting agenda.

It would also be expected that the people responsible in this way would have compliance with the authorisation as a part of their performance assessment and possibly their reward system. This is done, for example, by Albright and Wilson, where the performance of individual managers is assessed against compliance with authorisations (Environment Agency 1996a).

#### Maintenance

Maintenance of plant and equipment, including leak detection and repair, is an essential part of ensuring that all process and abatement equipment is functioning as intended. The sector is demonstrating a more proactive approach to maintenance. For example, Reliability Centred Maintenance adopted from the civil aviation industry has been used by Zeneca (Geraghty 1996) and Entwistle (1996) has summarised the benefits of total productive maintenance.

The benefits of the formal application of Leak Detection And Repair programmes in the US, involving leakage reductions in the range 50-80% for processes involving continuous production are also well documented, for example Scataglia 1993. There are also examples of staff engagement such as the Unusual Incident Reporting scheme used by Glaxo Wellcome which backs up routine inspection and maintenance and encourages all staff to be vigilant and report even very minor incidents such as weeping valves (Environment Agency 1996b).

The key point for the Inspector is that there is a management procedure in place to ensure that the process is working and continues to work within the design specification. There are various ways in which the Inspector can satisfy him/herself that this is so. For example, by examination of the management system and auditing monitoring and maintenance records.

## **Control**

Control covers many issues and there are even more ways of ensuring that control is maintained over the process. The main point for the inspector is that the process operator has identified the key environmental control issues involved, the associated indicators of performance and a mechanism for gathering, disseminating and responding to information on these indicators. This is a broad area and only a few examples have been given below.

Controlling the reaction to ensure that it remains within design parameters is a crucial point in ensuring that releases are minimised. Computer based monitoring of process performance and of discharges is widely practised and would now be BAT for new processes. But possibly more valuable is the existence and use of review procedures that ensure that the information available from such monitoring is used to improve plant performance. The more extensive use of computer monitoring and control is one aspect of this and a recent good practice guide from the ETBPP (1997a) illustrates such techniques applied to savings of energy costs but the same approaches can be used to control and optimise reaction yields and hence reduce wastes.

This sector is characterised by a rapidly changing throughput. Many operators generate information sheets (batch cards) to deal with specific batches. Incomplete batch cards or deviations from their requirements may indicate a potential problem.

It would be expected that the process operator has staff who understand the end-of-pipe monitoring data they are gathering and can detect trends and make recommendations accordingly. An understanding of the monitoring techniques used and potential alternatives could also be expected.

The impending introduction of the IPPC Directive in the UK means that for the first time raw material and utility use will be significant regulatory issues for process operators. Such issues may be particularly amenable to performance indicator approaches. Metering of utility use is an important measure of performance and in the future process operators could be expected to monitor utility use by specific processes. If they were significant consumers they could also be expected to implement monitoring of utility intensive process units.

Some process operators now link releases to the environment to actual production. This provides a useful measure of actual environmental performance and ensures that improvements in performance do not come about solely because of reductions in production. However, such an approach is generally more amenable to continuous operations rather than the batch operations characteristic of this sector. Care should therefore be shown in asking operators to develop such an approach, although for some a relatively high level linkage between, say, production and utility consumption may help identify products or activities that cause a disproportionate environmental burden.



There are many more potential control issues/performance indicators. Every process will have different needs and it is impossible to cover every eventuality. However, what can be expected, irrespective of the actual issues and indicators, is that all relevant information is regularly gathered together and reviewed. Process operators will already have self-monitoring requirements placed upon them, including a schedule for reporting to the Agency. This necessitates having a system in place to gather, collate and consider the data before its submission to the Agency. It could be expected that a similar approach was adopted for information that is largely of internal relevance. A number of process operators already do this on a monthly or quarterly basis.

## **Planning**

There may be opportunities to avoid or minimise releases resulting from careful planning and scheduling of process operations. Examples would be scheduling successive batches of oligomers in order of increasing molecular weight and avoiding waste washings by use of the same solvent in successive batches. These opportunities would be very process specific and the emphasis should be on the process operator to demonstrate that such opportunities have been considered.

Albright and Wilson (Environment Agency 1996a) produces an annual SHE plan that outlines its future environmental commitments. This draws together all its planning relating to the environment, not just that associated with the IPC authorisation. A process operator could be expected to demonstrate how planning with respect to the authorisation relates to wider environmental plans.

## **Waste minimisation**

There are many examples of the application of waste minimisation programmes in the chemical sector. They often show that such programmes pay for themselves through the savings they reveal. Examples of guidance and experience in this area, include:

- the 3Es methodology: Profiting from pollution prevention, which outlines the Agency's guidance on waste minimisation (HMIP 1994b);
- the regional waste minimisation clubs, for example the Aire and Calder Experience (March 1996);
- many publications on the subject (for example "Waste Minimisation - a practical guide" published by IChemE (1996)).

Ignorance of how to approach the subject can no longer be considered to be a credible excuse. A process operator would need to have a convincing reason for not undertaking a waste minimisation exercise and repeating it periodically at a frequency determined by the nature of the working practices at the process concerned.

The USEPA has also undertaken considerable work in this area (Bridges 1994) and Freeman (1992) has summarised the key components of the administrative framework for a waste minimisation programme.

## Designing the environment into the process

The process operator will almost certainly have an explicit procedure for initiating and approving new projects. As indicated in the introduction of this section pollution prevention is best introduced at the start of this procedure and the Inspector would want to be satisfied that this is what was done.

The procedures used for the approval of capital expenditure usually involve some form of financial consequence analysis and several companies include an environmental consequence analysis. For example, Zeneca has a mandatory system of SHE for all new or modified products or processes. These reviews take place before the start of formal SHE studies and are initiated at the conception of the product in the research department. At this stage during route selection the environmental impacts are assessed and compared. Once the product leaves the research department and goes into process development and subsequently manufacture the SHE reviews are continued and recycled if major changes occur. (Bradburn 1994).

ICI has also developed a SHE system for assessing the environmental implications of new developments (Jones 1993). This system is based on:

- identifying the target product;
- generating manufacturing route options after which a crude screen will be applied to identify the few that merit full laboratory testing;
- laboratory evaluation;
- select preferred manufacturing route;
- initial process development;
- siting decision;
- manufacturing site process development;
- initial manufacture;
- long term manufacture.

Consideration of environmental impacts at the earliest stage of project approval and the creation of a documented audit trail would now be BAT for new plant and significant variations to existing ones. It could also be expected that the environment manager, or equivalent, would be involved in signing off a project at all significant stages in its development.

Many process operators have now developed guidance for those involved in the development and implementation of new products showing how environmental considerations should be systematically built into the project's evolution. This guidance may be formally linked into a management system and may include checklists of issues that should be considered. Inspectors may wish to consider whether all appropriate issues have been included and that no presumptions are built into checklists that may restrict the imaginative search for alternatives.

Another part of the process development task is the selection of chemicals to be used in the process. Many companies have developed lists of chemicals which they either will not use or will actively avoid using. The existence of such lists is a positive indication that the company is taking a more proactive stance in relation to its environmental impacts which is clearly desirable. There may be scope for the Agency to encourage such actions, possibly by

developing a joint priority list with the CIA. Such a list could be linked to the priority list used for developing the CRI.

## Incidents

There are four key areas that process operators need to address when managing incidents. These are how they:

- respond to them;
- report them internally;
- report them to the Agency; and
- learn from them.

In terms of response, the process operator should be able to demonstrate a well defined management structure to deal with incidents. This management structure and any associated emergency response equipment should be regularly tested under 'real' conditions i.e exercises should not be confined to core operating hours. The frequency and extent of exercises will depend upon the hazard associated with the process. It is also possible to develop procedures to stop minor incidents becoming significant ones. For example, one company utilising large amounts of odorous compounds has developed a system whereby staff who notice an abnormal odour on site can notify a central control room of the problem. This provides the opportunity to deal with the problem before it give rises to an off-site problem.

Process operators can be expected to have in place a robust internal system for recording all incidents. Traditionally these have focused on health and safety issues but many now incorporate environmental incidents. An inspector could expect to see environment covered as a discrete area, whether on the standard incident reporting form, subsequent investigation or the preparation of summary statistics. It is important to recognise that process staff may need guidance on what constitutes an 'environmental' incident, particularly when there may be associated health and safety implications.

Process operators have a statutory obligation to report 'significant' incidents to the Agency but there is no guidance on how to interpret 'significant'. Glaxo Wellcome (Environment Agency 1996b) has developed, in consultation with the Agency, a mechanism for ranking incidents with an associated reporting 'trigger'. The system, known as the Spillage and Release Index, is based on the nature of the substance (toxic, oil, solvents etc.), size of the release (less than 10 litres, 10-100 litres etc.) and the fate of the spillage (contained in bund, contained elsewhere, released to surface water etc.). The development of similar guidance would appear to offer both the Agency and process operators considerable advantages.

Finally, process operators should have in place a system by which they can identify the key causes of incidents and, if necessary, implement improvements. Such a system should be integrated with the incident reporting mechanism and should allow the consistent delineation of trivial and non-trivial incidents. Non-trivial incidents should be ranked and an appropriate level of inquiry (process, site, company etc.) triggered. The involvement of the Process Environment Manager, or equivalent, is vital to the inquiry system. All inquiries should be minuted, actions, deadlines and resources assigned to individuals and regular follow up on progress made. For larger process operators a system would be of benefit whereby the results of such

investigations are disseminated on a site or company wide basis. One final issue to consider is access for the Process Environment Manager to information on all incidents. Some incidents may not have immediate environmental consequences but may provide evidence of future problems. It is therefore useful for someone with an understanding of the process' environmental impact to take an overview of all incidents and possibly be automatically included on the more significant incident boards of inquiry.

The IChemE is developing an accident database as a mechanism for disseminating information about the causes and responses to accidents. The database includes some information on environmental damage and this is being supplemented over the next few years (Bond 1996). The database may offer inspectors and process operators a useful source of information.

#### **4.3.2 Staff awareness and training**

This is an extremely important issue. There have been many examples in the past of companies striking a very positive environmentally responsible corporate position yet failing to deliver on commitments in their operational performance. This phenomenon has been referred to as "Green froth". With the growing use of publicly presented and externally audited corporate environmental reports and management systems this is less easy for companies to do.

A corporate positioning decision at Board level is one thing but staff have to feel that environmental issues are a high priority in the work they do for actual performance to improve. If all the staff involved in process design and operation do not recognise and feel that pollution prevention is something that will lead to personal recognition and success within their organisations it simply will not happen. It may be appropriate to build up a picture of staff awareness via brief interviews with selected staff. In such situations it may be worth bearing in mind that knowledge about an IPC authorisation often resides in the middle tier of management and that less awareness may be exhibited by those higher up or lower down the company structure.

It is difficult to be prescriptive about "best techniques" in relation to staff awareness and engagement but it is clearly BAT to have a workforce that is aware of the environmental implications of the tasks they do and how they should behave so as to minimise these effects. It is therefore relevant to expect staff to be aware of these issues when conducting inspections and to see evidence of the process owners devoting resource to staff training and to informing staff on the environmental performance of the process and the site.

There are a wide variety of approaches by which staff are kept informed. These may include regular cascade briefings, e-mail, annual reports, regular newsletters. Each process operator is likely to have their own approach to communication, the key for the inspector is that there is a system in place that identifies environmental issues relevant to the site, prioritises them and then communicates them effectively to appropriate staff members. Some companies have adopted schemes that reward staff who identify ideas for waste minimisation, improvements in housekeeping etc. This can be a useful way of demonstrating that environmental issues matter to the process operator as well as maintaining their profile.

The knowledge, experience, skills and motivation of the staff operating processes is obviously a key factor in performance and one that is relevant in considering an authorisation. Once again, however, attention needs to be paid to the results of the training rather than the detailed procedures companies use to train their staff. In order to work effectively in preventing pollution the Inspector would want to ensure that the staff involved are aware of the ways in which the process affects the environment and the effect that their actions have on this impact.

Any training needs to be supplemented from time to time. Glaxo Wellcome uses pocket sized "IPC awareness" cards to help with this. These cards are issued to all process staff and contain the main pollutants and the key abatement systems for the particular process area (Environment Agency 1996b). Staff should also be aware of the company's objectives in relation to the environment and the current corporate, site and process performance in relation to these objectives. At Albright and Wilson all staff are given a book on safety, health and the environment outlining legal obligations and practical examples of do's and don'ts (Environment Agency 1996a).

Training is the means by which any gaps in the key knowledge and competencies are filled. In order to ensure that suitably experienced staff are being used the company would be expected to identify the environmentally critical tasks in the process, identify the knowledge and experience required and any deficiencies with appropriate steps to make good any deficiencies identified. Positions that may require some form of specific environmental training include process managers, shift foremen, auditors, plant designers and research chemists. The company can reasonably be expected to keep training records. The Inspector may find it useful to establish that such records exist and to look at them from time to time.

In addition to job specific training, all new staff should receive an environmental briefing during their initial induction. This briefing should as a minimum inform staff of the existence of the IPC authorisation and the legal obligations associated with it. During site visits a number of companies noted that the National Rivers Authority's video on preventing water pollution was a useful tool for informing new staff and indicated that they would welcome the development of a more up to date version covering the environment as a whole.

#### **4.3.3 Discipline**

The main issue of concern in relation to discipline is how effective are the procedures in practice. The existence and evidence of the use of the company's disciplinary procedures and whether they include environmental impacts as one of the results of negligence would be one aspect the Inspector might consider. Another would be to audit the examination and implementation of any actions taken as a result of pollution incidents or public complaints.

An important factor in several major industrial accidents in the past has been the communication problems occurring at shift handover. Hints about the avoidance of such communication problems from an occupational psychologist have been produced (Lardner 1996). Formal procedures should exist to ensure that such handover problems do not occur. A number of informal methods such as the use of wipe boards are widely used but these should not compromise more permanent and traceable communication, either paper or electronic.

Ashton (1997) has also explored the implications for health and safety, and by implication environmental, management of the moves to devolve greater responsibilities from corporate bodies to individual processes. This work suggested that problems should not arise provided health and safety (and the environment) are assigned a high priority during re-organization.

#### **4.3.4 Resources**

Three resources are considered:

- financial in relation to investment;
- physical;
- accounting.

#### **Financial**

One key point in relation to financial resources is whether investments primarily motivated by environmental concerns are considered and given proper consideration alongside other investment bids. It might be pertinent to enquire about the criteria used by the company to sanction investments and to consider the current investment plans for the process/site.

A further issue is the trend in the sector to devolve responsibility to operational (process) units with greater emphasis on unit rather than total corporate profit. This may contribute to increased pressure to reduce manning levels, maintenance and investment. Conversely it may aid the identification of the true financial and environmental costs associated with a particular process.

Since equipment and services are often supplied by contractors it is also important to consider what criteria are used in selection and purchasing decisions. These relate primarily to the potential environmental consequences of the materials and services supplied, such as the long term durability and security of tanks and pipes.

#### **Physical**

From the Inspector's point of view the key points are that process operators are aware of their use of water and energy and that they periodically consider their use by benchmarking their performance with others or by conducting audits and studies to identify savings.

Efficient use of physical resources is a factor that will apply to authorisations under regulations to be established to meet the requirements of the new IPPC Directive. It is also a factor that might need to be considered currently in comparing options under a BPEO assessment.

The CIA has recently reached agreement with the Department of Environment, Transport and the Regions (DETR 1997) to reduce energy consumption in the chemical industry by 20% by 2004, using 1990 as a baseline. The DETR will fund consultancy for SMEs to help them reduce their energy use.

There has been a substantial move towards CHP (combined heat and power) in the chemical industry and currently approximately 60% of the chemical industry's power needs are met by CHP. The introduction of CHP can lead to both environmental and economic advantages. For example, the recent introduction of a combined heat and power plant at Zeneca's Huddersfield site is estimated to save the site £2.5M per year in energy costs. The plant involved a £10.6M investment and involves a 16MW combined cycle combined heat and power facility. It is anticipated that the new plant will reduce the emissions of carbon dioxide, sulphur dioxide, nitrogen oxides and particulates (AHS Emstar 1997). However, this large site is not indicative of the general size of process that is likely to be found in this sector. Caution should therefore be exercised in extending CHP to smaller processes where the investment costs may not be justified and the experience to operate them may not be available.

As a broad rule of thumb the key requirement for the successful introduction of CHP is a heat to power ratio of at least 1:1, the heat requirements can be greater than the power but it is not usually economic if they are less. There also needs to be a requirement for power extending over most of the year i.e. >6000 hours. The average total energy needs should be greater than 45 kW and below 3MW the most economic approach is to use a gas engine. Above 3MW a gas turbine is more efficient but this depends on a range of factors including the heat requirements.

There are similar examples in savings resulting from water audit studies. For example from the inorganic chemical sector, MEL Chemicals showed savings of over £50k per year from a saving of 10% of water use, as a result of a water use audit and study (Fairhurst 1994). It is relevant to note that the German regulations for waste water discharges from the chemical industry require that waste water minimisation is undertaken at all sites as part of any application for an authorisation.

## Accounting

Another relevant aspect of resourcing is the approach taken to cost allocation. All modern management accounting systems attempt to improve cost allocation to specific business functions. It is not uncommon, however, for environmental costs to be only poorly attributed to specific activities and instead to be treated as part of an operational overhead, for example, in the use of a site charge for solid waste disposal, or maybe as an exceptional item to cover the cost of the clean up of contaminated land.

Clearly the better the understanding there is of the true costs of different processes the more obvious are the cases for seeking savings. It follows that BAT would seek to assign all environmental costs as precisely as possible to the processes involved. In particular there should be no hidden costs for a particular process which, for example, does not have to pay the costs for collection and disposal of the solid waste it produces because it is mixed in with another waste. Such practices do not encourage recycling or reuse. However, while it should generally be possible to identify the environmental costs associated with a process it may be difficult to develop a further link to specific batches.

Some examples of environmental costs borne by businesses taken from the USEPA (1995a) are given in Table 4.3 below.

**Table 4.3 Some environmental costs borne by industry**

Regulatory and operational		
Notification	Reporting	Insurance
Fees and taxes	Waste disposal	Closure de-commissioning
Monitoring	Environmental technology	Inspections
Contingent costs		
Penalties and fines	Redemption	Property and personal damage
Image costs		
Insurers	Customers	Local community
Investors	Suppliers	Regulators

Taking cost attribution further there has been much talk about the use of full economic cost accounting, particularly in the USA. Full economic cost accounting seeks to include the external or societal costs into the costs borne by companies. Although one attempt has been made to apply this technique, also in the USA, its application involves many contentious assumptions and is still basically at the research stage. It seems unlikely to develop rapidly enough to be of any practical consequence in the short to medium term.

#### 4.3.5 Time

Inadequate time to do things properly with consequential increased wastes or risks of waste will be a major concern of Inspectors. The tangible manifestations of these concerns will be aspects like:

- reduced manning levels;
- scheduling and frequency of batch runs and the relationship of waste production to run time;
- records of waste production from batches;
- records of time spent in development and testing of new practices.

#### 4.3.6 Senior management commitment

There are several means of discerning the expressed commitment at senior management levels to the environmental impact of the organisation. The publication of a corporate environmental report, being accredited to ISO 14001 or to EMAS and being a signatory to the Responsible Care programme are all external manifestations of senior management commitment.

The key point, however, is whether this commitment is communicated, felt and shared by the staff who have to make decisions that affect pollution prevention from the process. In other words, as with the other issues discussed here, the Agency should look to the results of the environmental performance of the company rather than the systems and procedures they



choose to use. Reporting environmental information can also send messages within the company that they are serious and committed. For example, at BP (Environment Agency 1996c) the SHE system is steered from the main board and responsibility is built into line management. Part of the procedure involves each business unit manager producing a formal annual report describing:

- management of key SHE risks in the unit;
- compliance with legal requirements;
- progress with policy implementation;
- progress against performance targets and objectives;
- next year's programme.

These reports are passed upwards through line management. The final product is a report from the group chief executive to the SHE audit committee which is a formal part of the board containing only non-executive directors (Read and Yeldham, 1997). Other companies have adopted similar procedures.

“Responsible Care” specifically commits a company at Chief Executive level, to “manage its activities so that they present an acceptably high level of protection for the health and safety of employees, customers and the public and the environment”. Specifically the principles of Responsible Care require a company to:

- assess the health safety and environmental impacts of its activities, products and processes;
- conform with statutory regulations as a minimum and work with authorities to develop and implement measures where needed;
- make employees and contractors aware of the commitment and involve them in its delivery;
- be open with information both inside and outside the organisation.

Adoption of these principles, whether via the Responsible Care programme or not, would appear to be BAT for the management and operation of processes in this sector.

In addition to adherence with these principles many companies now set themselves objectives at a corporate level to reduce releases of specific chemicals (or chemical classes) and to minimise use of resources. The establishment of release inventories is part of the IPC authorisation requirement so is BAT for all processes. The setting of targets for reduction and reporting of this, at least within the company, so that process operators appreciate the effect of their work, also appears now to be BAT for the management of such processes. Environmental performance indicators (EPIs) are widely used in the sector and would now appear to constitute BAT, although, as is argued below, the existence of EPIs is less important than the commitment to improve performance and the use of systems to measure and report this performance.

In order to make environmental data easier to understand and to follow they are often converted into environmental performance indicators. Such indicators often comprise two

statistics one related to an emission or an environmental effect and the other to a level of activity. Categories and examples of such indicators are given in Table 4.4 below.

**Table 4.4 Examples of environmental performance indicators**

Category of environmental performance indicator	Examples of indicators
Measured environmental impact	Changes in species diversity around site
Risk of impact	Usage of priority pollutant chemicals
Emission or waste measure	Total VOC emissions to air
Resource consumption	Electricity use per unit of production
Input of effort to alleviate impact	Money spent on SHE training per employee
Efficiency measures	Percentage utilisation of raw materials
Third party responses	Number of neighbourhood complaints
Financial	Investment in capital environmental equipment

Many indicators can be chosen but the most valuable ones from the Inspector's perspective are those that are output measures rather than input ones. Levels of, and changes in, emissions are far more directly relevant than say investment in equipment or training. As with the other management techniques the Inspector needs to concentrate on the effectiveness of the techniques used not the aspiration or intent.

The wide variety of chemicals used by this sector poses special problems in assessing environmental impact for reporting and other purpose, such as determining BPEO from a number of alternative options. There is no unequivocally correct answer to this problem. ICI has recently adopted an environmental burden approach that has many basic similarities to the proposed BPEO methodology of the Agency, being based on a ratio of load to an environmental quality standard (ICI 1997). Other chemical companies such as Dow have chosen a priority group of chemicals and target their reduction programmes on these as a group. The important issue is that the company has set targets for reduction of wastes and has, additionally, some procedure(s) in place to ensure that the reduction programmes do not mask increased environmental impacts or risks due to underlying increases of more hazardous chemicals that may have been overlooked in the aggregation process.

#### **4.4 Operator and pollution risk appraisal (OPRA)**

The operator performance part of the Agency's Operator and Pollution Risk Appraisal (OPRA) scheme contains several elements discussed earlier in this section (Environment Agency 1997a). The seven specific attributes considered as part of the operator performance in OPRA are:

1. Recording and use of information.
2. Knowledge of regulations and authorisation requirements.
3. Plant maintenance.

4. Management and training.
5. Procedures and instructions for process operation.
6. Frequency of incidents and complaints.
7. Auditable management system.

The recommendations made in the earlier part of this section indicate that processes in this sector operating according to BAT would all score highly in the relevant management aspects of operator performance under OPRA.

#### **4.5 Conclusions**

In summary the sector on the whole aspires to be environmentally responsible and the leading companies often aim to, and achieve, improvements in environmental performance that outstrips regulatory requirements. Frequently such improvements have gone hand in hand with cost savings. However, the sector is not homogeneous and not all companies aspire to the higher environmental performance ground. In addition, some that establish and commit at a corporate level to this higher performance sometimes fail, in practice, to deliver it.

Effective management requires an active process of establishing objectives, setting targets, making measurements and revision in light of the results. Use of these processes in the management of the environmental impacts of organic chemical processes would be BAT but there are clearly various ways of achieving this and it is not possible or desirable to select one specific approach such as EMAS registration as the technique to use. The key issue for the Inspector would be evidence that the active process outlined is underway and that such procedures are in place and are being monitored and reviewed - in short that the process owner has recognised the environmental implications of the process and is managing them effectively.



## 5. PROCESS TECHNIQUES

This chapter of the report considers some of the process techniques that may be available for preventing and/or controlling pollution. Such is the complexity and diversity of the sector that it is not easy, nor is it desirable, to be prescriptive about process techniques. Instead a high level approach has been adopted which discusses some of the key environmental implications of using the following manufacturing units:

- storage and handling of raw materials, products and wastes;
- plant systems and equipment (e.g pumps, compressors, relief valves, valves etc.);
- reaction;
- separation; and
- purification.

It is important to note that most processes will not utilise all of these manufacturing units, indeed where they do apply them, it may be in a manner that is very different from the general discussion presented below.

Notwithstanding these limitations it has hoped that this section can provide a framework within which inspectors and process operators can discuss the complexities of a particular process and how pollution can be prevented and minimised at source.

Section 2 and Appendix B of this report provide more information on how different types of process may deviate from the broad discussion of manufacturing units utilised in this section.

### 5.1 Storage

Storage incidents are comparatively rare but where they have occurred they have often given rise to significant environmental harm.

To a large extent the approach adopted towards storage by a process operator will depend upon the inherent properties of the raw materials, products and wastes that are being stored (e.g toxicity, environmental persistence etc.), the quantities involved and their proximity to sensitive environmental receptors.

Given the large number of raw materials, products and wastes handled by the sector, it is impossible to cover every possible combination of inherent property and receiving environment. However, a large body of information does exist covering the inherent properties of materials (e.g Hazard Datasheets) and these can act as a useful first screen for inspectors in identifying areas of particular interest.

In certain instances these properties and the local environment may be of such a combination that only a major capital storage scheme can adequately protect the environment. However, in the majority of cases it is likely that much can be done to minimise both routine and non-routine emissions via relatively simple and inexpensive measures such as labelling tanks and valves and painting tanks.

Storage areas are subject to the same risks of overpressure, leakage, equipment failure as the main process areas. The distinction in the case of storage areas is that the material inventories, and hence the potential hazards are greater and the level of surveillance is generally lower. For storage, as for main plant, there is thus a need for the application of hazard and operability (HAZOP) studies, for the structured review of over pressure and underpressure relief arrangements and for effective measures to be in place for the mitigation of the effects of routine and non-routine releases. Dispersion modelling and risk assessment might be required to demonstrate the acceptability of direct releases to atmosphere.

### **5.1.1 Liquid Releases from storage**

Liquid releases from storage may occur in five main ways. These are:

- drainage systems surrounding storage sites;
- dry storage;
- drum storage;
- tank storage; and
- tanker loading and off-loading.

Each of these is discussed in more detail below.

#### **Drainage Systems**

Storage areas are often open to the elements and thus runoff can mobilise any leakage, spills etc. that may arise from storage activities.

As far as is practicable, effluent and runoff collection systems should be kept separate in order to minimize the quantity of effluent requiring treatment. It may be appropriate to ensure that the different systems are readily identifiable to all those involved in their use and maintenance. Different coloured paints could be used to differentiate the systems. It should be appreciated that non-routine incidents may occur in the dark and/or inclement weather and may involve individuals from the emergency services who may be unfamiliar with the systems. Such situations, where a rapid response may be required, may be dealt with more easily if the respective systems can be discriminated readily. The use of separate systems also maximises the chances of pre-treatment or beneficial recovery of some of the components, particularly those from major spillages.

Whenever hydrocarbon oils are stored oil separators may be required. The Agency has issued guidance on the use of separators (Environment Agency 1997b). Oil separation should usually be done close to the point of arising and be the subject of a regular visual check of performance.

As far as possible all lines, including drainage lines should be run above ground so that leakage is immediately detectable. The assumption should be made that all underground drains will leak and the consequences should be assessed i.e the inherent properties of the compounds that may be present in the drainage system and the proximity of the drainage system to surface and groundwater.

The UK has a number of large chemical sites where several different companies may be operating processes. It is particularly important on these multi-user sites that responsibility for site drainage is clearly defined and that all those who utilise the system do so within a common operational framework.

These principles apply equally well to storage in plant process areas.

### **Dry storage**

Organic chemical compounds will burn so that there is always a fire risk during dry storage. In addition, some organic powders, when present in finely divided form are an explosion risk. If fire or explosion occur it is likely that fire fighting water will have to be applied to prevent expansion of the damage. This fire fighting water may mobilise the stored materials and release them to the local environment. Developments in solids handling and transportation have led to the increased use of IBCs, tote bins and large bags of up to a tonne capacity. These have the potential for greater quantities of spillage than would have occurred from bags on pallets.

The process operator should consider ways of:

- minimizing minor leaks and spills within storage areas, which are likely to be mobilised in the presence of a small amounts of water. Buildings should be constructed to minimize dust traps and floor areas should be kept clean. Damaged sacks should be rebagged or put into other containers as soon as possible. Adequate control devices should be in place to deal with leaks and spills. When leaks and spills are washed away the wash water should be directed to the effluent treatment system and not allowed to access any separate drainage system;
- ensuring that major leaks and spills and fire fighting water can be directed to a tank or basin where they can be held for monitoring prior to a decision being taken on how they should be disposed of or, as may occasionally be possible, recycled;
- ensuring that large containers and bags have adequately sealed openings with valve caps, locked valves, secure lids and, where necessary, that appropriate venting is supplied.

Consideration should also be given to how dry materials are segregated from incompatible materials or potential heat/energy sources.

### **Drum Storage**

Drum storage is extensively used in the chemical industry. Much of this storage will be bulk storage in the open.

Drums should generally be stored in a concrete hardstand with a kerbed retaining wall to prevent any contamination running directly to storm water drains. Runoff from the hardstand should be passed to a holding tank for monitoring prior to disposal. Drum damage and leakage is comparatively rare so it is likely that most water run off from the storage area can be disposed of via the site drainage system. Procedures should be in place to minimise the number of drums

held outside these central storage areas. In addition, consideration should be given to minimising overall drum storage inventories on site, for example by utilising 'just in time' ordering.

Routine measures should be in place to protect drums from damage, such as avoiding storage close to traffic flows. Care must be taken to ensure that safeguards are in place to avoid overpressure if drums have to be maintained at higher than ambient temperatures or if heat is required to mobilise the contents of the drums.

In general metal drums that are to be stored for any length of time should not be in direct contact with the floor. This minimises the risk of corrosion adversely affecting the drum's integrity. In general, drums should not be stored on site for any length of time.

Routine inspection should ascertain, not only the physical state of the drums but also whether all of the materials are for current use and required. A system should be in place for identifying, returning or disposing of old, superfluous material. All labels should be legible and the date of storage might be marked if limited shelf life is likely to be a problem.

A separate area should be used for drum cleaning. Clearly, the less material left in a drum, the fewer the problems generated during cleaning. Drum emptying arrangements should be used to maximise liquid removal. For example, for certain viscous liquids heating of the drum during emptying may reduce the residual left behind. Spray cleaning is preferred in order to minimise the quantity of effluent produced. Wherever possible washwaters from drum cleaning should be retained for reuse. Waste water from drum cleaning forms part of the effluent load. It can represent a significant and variable part of that load so that process operators often prefer to sub-contract drum cleaning to specialist companies. If this course of action is taken, it is important that checks are carried out to provide assurance that the sub-contractor is conducting the operation in an appropriate manner.

## **Tank Storage**

The most commonly encountered bulk storage of chemicals is as liquid in storage tanks. The potential for harm is significant because of the large inventories involved and the fact that escape can often continue for some time unobserved.

The general principles of design and operation of tank storage are aimed, first, at containment within the equipment and then, in the event of a release, at ensuring protection of surface and groundwater. Finally there must be the capability to deal with the contained release either by recovery or disposal. To achieve these objectives a rigorous assessment should have been made of the risks, probabilities and consequences using HAZOP techniques. Attention should also be paid to management techniques as well as to equipment design, for many of the recorded storage incidents are attributable to human errors relating to overfilling and damaging flexible hoses.

A comprehensive framework of advice on protective measures to be taken against loss of containment from storage tanks can be found in existing Environment Agency guidance, for example:



- Pollution Prevention Guidelines (PPG) 2 - Above ground oil storage tanks (EA 1997c);
- Pollution Prevention Guidelines (PPG) 18 - Fire Fighting Water (EA 1997d)
- Masonry Bunds for Oil Storage Tanks (EA 1997e);
- Concrete Bunds for Oil Storage Tanks (EA 1997f).

In general it is recommended that bunds should not have a direct connection to drainage. Rainwater should not be allowed to accumulate in the bund. It may be appropriate to install a level marker in the bund to indicate when rainwater should be removed. Where visual inspection of the bund is difficult or the stored compound is particularly hazardous it may be appropriate to install level alarms.

Any storm water removed from the bund should be monitored prior to removal. The parameter monitored should be commensurate with the stored compound. Thus for acid or alkali storage pH monitoring may be appropriate. When the rainwater is uncontaminated it can be directed to the site drainage system. If contamination is detected then the water removed should be sent for on or off site treatment and the cause of the contamination investigated.

Chemical compounds which are incompatible with each other should never be stored in tanks in close proximity. There are obvious dangers if compounds were to be mixed as a result of leaks, tank failure or off-loading to the wrong tank which, on mixing, produced violent reactions or emitted toxic vapours.

As with dry storage consideration should be given to the fire risk associated with storage tanks and the need to ensure that credible volumes of fire fighting water that may be used can be retained.

There may be cases where different standards or methods of containment might be appropriate. Examples are where:

- risk assessment verifies that full bunding is not required;
- the high flammability of the material stored makes it impossible to allow accumulation of material close to the storage area;
- the toxicity of the material demands immediate emergency measures such as dilution or neutralisation.

Consideration should also be given to the volumes of liquids stored in tanks on-site. Wherever possible inventories should be minimised, although it should be appreciated that potential measures such as 'just in time' ordering may result in increased traffic movements and loading/unloading which may increase the risk of spills.

### **Tanker Loading and Offloading**

Loading and offloading areas of road and rail tanks should be concreted and graded to prevent spillage running to storm water drains. "Sleeping policemen" are often an inexpensive way of securing the area.

Flexible hoses are a vulnerable point in loading and off loading activities. They are susceptible to failure as a result of damage or from movement of the tanker while the hoses are connected. For these reasons, excess flow automatic shut-off valves should always be fitted to the fixed part of installations connected by hoses. A schedule should exist for hose testing and examination and the hoses should be tagged to demonstrate compliance.

All tanks, valves, unloading bays etc. should be clearly marked as to the material which they may accept. In addition, adequate lighting of storage areas should be provided to avoid the risk of incorrect connections or accidents.

### **5.1.2 Emissions to air from storage activities**

Storage related emissions to air may arise from:

- drums;
- storage tanks; and
- sumps.

Each of these is discussed below.

#### **Drums**

Most drum storage is not enclosed, so flammable vapours will not accumulate in the rare event of a leaking drum. Protection from excessive heat from sunlight might occasionally be appropriate when particularly volatile liquids are being stored.

The filling and emptying of drums is likely to displace volatile organic materials. If large amounts of VOCs and/or particularly hazardous compounds are in use then ventilated filling booths or suction heads at the filling point should be used to remove and then to collect the vapours for recovery or abatement.

#### **Storage Tanks**

Measures to be taken to suppress emissions from storage tanks should be commensurate with the volatility of the tank contents and the potential harm (human and environmental) of the emissions.

Emissions to atmosphere from storage tanks arise as a result of:

- displacement caused by changes in the ambient temperature;
- displacement from tank filling;
- the use of inert gas blankets as fire or contaminant protection.

Measures which can be considered to minimise these losses include:

- insulating or painting the tanks to reduce solar gain and temperature fluctuations which lead to breathing losses;

- back venting vapours to tankers or to the process when filling or emptying. This is usually economic for tankers close to the storage area but may not be practicable for the connection between storage tanks and the usually more distant reaction vessel;
- ensuring tight control of inert gas feed to blanketing spaces. The normal method of achieving this is the use of pressure-vacuum valves;
- fitting high level alarms to prevent overfilling;
- fitting floating roofs to the tanks. Floating roofs can reduce vaporisation losses but do have vapour losses from wetted sides and do allow rain to run into the tanks. Floating roofs are not normally an economic solution for tanks less than 1000 m<sup>3</sup> and their effectiveness is dependent on good maintenance. Floating roofs may also give rise to a contamination problem when a tank is used to store several different chemicals;
- absorbers, adsorbers and condensers can be fitted to the vent systems but they are often too distant from the main process services to be deployed economically;
- closed, pressure vessels will be used for highly volatile fluids or for material which is volatile and highly toxic.

Occasionally storage tanks are emptied and cleaned to remove build up of solid contaminants, for change of use or for entry and inspection. This is an infrequent event which will almost inevitably generate emissions to atmosphere as well as quantities of solid and liquid waste. These operations should be planned. The plans should be devised to minimise the environmental impacts and the disposal routes should be established within the company procedures before the operation is begun.

## Sumps

The use of a blanket of plastic balls has been proposed as a method of limiting evaporation from the surface of open sumps and baths. This is only effective in very still conditions. Movement within the liquid can move the balls of the blanket and result in a greater evaporative surface than if the balls were not present. If a sump's contents are sufficiently static for the balls to be effective, the need to store the liquid so long should be queried. Storage is not normal in sumps but oily waste often accumulates in oil water separators. Good practice is to skim the oil frequently so there is no accumulation.

## 5.2 Plant Systems and Equipment

The objective of this section is to discuss the environmental aspects of some of the design and equipment features that occur in most plants and in most of the sections of those plants. The most significant issue is that of fugitive emissions and how these can be minimised.

### **5.2.1 Ventilation systems**

Many small tonnage, multi product, plants are enclosed within buildings. Effective ventilation is required to prevent the:

- build up of toxic material;
- accumulation of flammable material.

The ventilation system will discharge at a safe height above the roof. Consideration will need to be given to:

- the load on the atmosphere of the evacuated contaminant;
- whether the resultant contamination of the roof is such that rainwater from the roof should be diverted to the effluent treatment system;
- whether the ventilation system should be fed to an abatement technique, although some such techniques may not be appropriate for dealing with large volumes of air containing low concentrations of contaminants.

### **5.2.2 Fugitive Emissions**

Batch processing offers numerous opportunities for fugitive emissions and the following sections identify a number of potential sources of such emissions. For example, during sampling, cleaning, change round from batches, cleaning, depressuring and purging. It is important that a procedure is in place for identifying these sources, monitoring the losses and, if necessary, developing and implementing an improvement programme. The USEPA has issued guidance on leak detection and repair (LDAR) procedures (USEPA 1984, USEPA 1994a) that may be of assistance in addressing this problem.

### **5.2.3 Overpressure**

Many reactions undertaken in this sector involve elevated temperature and/or pressure. In such situations there is always the possibility that over pressure within the reactor may occur under abnormal operating conditions. It is important that such over pressure is dissipated as rapidly as possible to prevent the risk of explosion which may have both safety and environmental consequences. Etchells (1996) reviewed 135 exothermic runaway reactions, mainly in batch reactors, reported to the HSE between 1986 to 1991. The results of this review are summarised in Table 5.1 below.

**Table 5.1 Main causes of runaway exothermic reactions reported to HSE**

Cause	Percent
Mischarging of reactants or catalysts	27
Little or no knowledge of reaction chemistry/thermochemistry	15
Inadequate temperature control	13
Inadequate agitation of reacting materials	12
Raw material quality	9
Inadequate maintenance	8
Operator error	4

It would be expected that a fully comprehensive, professional design procedure had been followed to establish the protection systems against overpressure of the equipment. This procedure requires the identification of all conceivable relief cases, calculation of relief rates, selection of relief methods, design of the vent system, discharge and disposal considerations and dispersion calculations.

It is important that management systems are in place to ensure that details of all relief systems are maintained in a register and that proper procedures are in place to ensure testing and maintenance at the appropriate intervals. In addition, procedures should be in place to prevent plant alterations which would invalidate the integrity of the protection system. In this context, the protection system includes all of the items in the design assumptions of the relief case. These might include items such as restrictor orifices, control valve trims and non-return valves.

Consideration needs to be given to the safe disposal of vented material. Emergency venting might be through an absorption system, to a dump tank or directly to atmosphere. If direct atmospheric venting is used, dispersion calculations will be required to demonstrate that harm will not be caused. If absorbers or dump tanks are used, additional design studies are required to ensure that the pressure drops in the system are compatible with effective operation of the safety devices. A problem that should be addressed is that of ensuring that abatement equipment installed in the vent system is maintained in a state of readiness even though the system is rarely used. It is vital that the relief system is designed to cope with the correct conditions; under some emergency situations the vented stream might be liquid or a two phase foaming or boiling mixture which would impose a different set of design constraints.

Most reactors make use of some kind of relief valve or bursting disc but occasionally inherent protection may be designed into the process to prevent the need for a mechanism that directs the over pressure to the external environment.

### **Inherent protection**

It is sometimes possible to avoid the need for relief systems. Possible approaches to this include:

- designing the system such that it can withstand all potential sources of high pressure;

- demonstrating from hazard analysis that the probability of overpressure is so low that protection is not required;
- utilising high integrity instrument protection systems, validated by risk assessment and hazard analysis;
- accepting that equipment failure will occur and containing the consequences. This is a method sometimes adopted for small scale laboratory operations.

## Relief Valves and Bursting Discs

Apart from atmospheric systems with open vents to provide relief, most reactors will use either relief valves or bursting discs to provide emergency relief. These systems are intended as a protection of last resort to function only when all of the other protection devices of trips, controls and alarms have failed.

The probability of use should therefore be extremely low which gives scope for discussion of the balance between the likely impact of a discharge against the need for installation of equipment to collect and treat the release. For example, when particularly hazardous substances are present in the reactor it may be appropriate to install a dump tank to accept the reactor's contents in the event of over pressurisation. Dump tanks will need to be professionally designed to withstand and capture the emissions from any credible over pressurisation incident in the reactor but typically may be expected to have a volume many tens of times greater than that of the reactor. Dump tanks should also be designed to allow them to be readily cleaned and any wash waters collected and sent for on or off site treatment.

It is sometimes appropriate to install a small capacity relief valve discharging to treatment systems to cope with, say, blocked in conditions and a large capacity device without containment to deal with fire.

Relief devices should never be installed as part of the control philosophy. The specific choice of the relief device to be used can be complex and influenced by consideration of such things as corrosion, solids deposition, need for integrity and explosion risks.

Both relief valves and bursting discs can be leak free if installed under a system of careful and competent maintenance. Both can be prone to leakage if maintenance standards are allowed to slip. It would be expected that some procedures for the checking for leakage from relief systems would be in place. Relief valves have the one great advantage over bursting discs that they will reset and so limit the discharge once normal pressure has been re-established. The resetting is unlikely to be leak free and the valve should be scheduled for urgent maintenance.

Both relief valves and bursting discs can be a source of fugitive emission and the inspection of the vent system for fugitives should be part of a plant management routine. In order to combine the advantages of both types of protective device, relief valves are sometimes mounted downstream of bursting discs. This can give a false sense of security. A pinhole leak in the bursting disc will promote leakage from the relief valve but cause a pressure build up that prevents the functioning of the bursting disc unless a vent is provided to the space between the

two. A pressure gauge should be installed to warn of this condition. An inspection routine is required to ensure that the warning is heeded.

High melting point and subliming materials pose particular problems to relief system design. A coating of solid under the valve or disc will prevent relief at the correct pressure. A plug of solid in the relief tail pipe, originating from a leaking valve or disc, will also disable the relief system and leave the vessel unprotected. Special measures would be expected to be in place in such situations to assure the integrity of the relief system such as heating, purging or increased instrumentation or inspection.

#### **5.2.4 Vacuum Systems**

There are five methods of producing reduced pressure conditions, two 'wet' and two 'dry', and steam stripping, which is not usually considered as a vacuum application. The selection of which method is appropriate for a particular process will be an entirely site specific one. This section therefore considers the main environmental impacts associated with each method.

The load on the vacuum system and the associated loss of material depend upon the degree of cooling and condensation achieved upstream and on the quantity of gas the system is required to handle. It should be noted that large quantities of non-condensable gas in the system inhibit the performance of condensing heat exchangers and increase the carryover from absorbers. A large component of the non-condensable gas is air which has leaked into the system through the seals of valves, flanges, agitators and pumps. Careful design and choice of equipment can reduce the number of sources and a high standard of maintenance can reduce substantially the ingress through the remaining seals.

Sufficient instrumentation should be installed to ensure that information is available to detect a drift in standards and allow remedial action to be taken. Simple logging of the time taken to produce the vacuum might suffice or more detailed analysis of the heat exchange performance. Clearly this is of less significance environmentally if additional downstream treatment is installed.

The Environmental Technology Best Practice Programme (ETBPP) has recently brought out a guide which identifies a number of techniques for optimising the use of vacuum techniques in a process (ETBPP 1997a).

#### **Steam jet ejectors**

Steam jet ejectors are simple and reliable and so are widely used in the sector. For low pressures, multi-stage ejectors are required. As many as six stages have been used to produce very low pressures but the use of more than three stages is rare. A compression ratio of <6 per stage is normal. They tend to be an energy intensive approach to producing a vacuum.

Condensing is usually by water jet. Condensable and soluble contaminants flow with the discarded water to form a low concentration effluent stream which may require the use of oil separation equipment. Non condensables are dispersed to atmosphere. The potential for the production of large volumes of diluted effluent during direct condensation has led to the development of surface condensers. This not only gives more potential for treatment or

recovery of the condensed process flow but also offers the potential for lower condensing temperatures and correspondingly more effective operation.

### **Liquid Ring Pumps**

The pressure is limited by the vapour pressure of the sealing fluid (which needs its own cooling loop). The contaminants in the gas stream partition between the gas stream and the sealing liquid. Contaminants in the liquid seal fluid may be amenable for recovery or the purge stream might form a more concentrated effluent flow. There are more choices for downstream treatment than in the case of the effluent from steam ejectors.

Both steam jet ejectors and liquid ring pumps have the potential to cause a severe noise problem unless suitable abatement measures are installed and this will need to be considered for operator protection as well as for the off-site impact.

### **Dry vacuum pumps**

Considerable advances have been made in recent years in the application of dry pumps for vacuum duties. Dry pumps are rotary pumps which rely on high rotation speeds and close tolerances to affect a seal. For high vacuum duties multi-stage arrangements are used. Unlike the other vacuum producing methods, these pumps do not introduce additional environmental impacts due to releases.

### **Steam Stripping**

In a system which is not water soluble, the use of steam stripping to remove lighter components is a cheap and effective way of lowering the partial pressure of the volatile component and achieving a lower temperature separation. Although intended for use with material which is insoluble in water, the overhead condensate will inevitably be contaminated and will need treatment.

## **5.2.5 Pumps**

The range of mechanical equipment associated with fluid movement and transfer is immense. Many items have been developed to deal with particular problems, and, in general the choice of machinery will have been made to meet the technical needs of the duty.

Traditionally pumps have been based on one of two systems: centrifugal pumps and reciprocating pumps, respectively, but from the standpoint of assessing their environmental impacts it may be more appropriate to categorise them as those which:

- are liable to leak all of the time;
- are liable to leak heavily on failure;
- never leak.



Pumps driven directly by a shaft require some form of seal to prevent the process fluids escaping to the outside environment. The traditional method of achieving this is the packed gland which is used for both rotating and reciprocating shafts. The seal is made by packing a soft malleable material into a gland housing which surrounds the shaft.

An advance on the packed gland for use with rotating shafts is the mechanical seal. The actual sealed joint between the static and the rotating part of the machinery is made by the close contact between two annular rings of metal, ceramic or graphite material. One ring is fixed to the casing of the pump; the other to the rotating shaft. The seal is maintained by spring loading of the joint.

In all seals with rotating or reciprocating shafts, lubrication of the seal is by fluid passing over the sealing surfaces, albeit at a very low rate. There is always, therefore, a leakage to atmosphere of the process fluid from a single seal if there is a positive pressure on the process side. If the pressure differential favours air ingress to the system, the air flow will often hasten wear on the seal and actually cause an increased leakage rate.

To prevent leakage of process fluids, double mechanical seals are used in a back to back arrangement. Pressurised sealing fluid is supplied to the space between the seals. Small quantities of the seal fluid then leak into the process fluids. This fluid usually requires an additional cooling loop. This arrangement has to be used if abrasive solids are present in the pumped fluid. Mechanical seals are widely used. They are generally reliable and leak free provided that:

- the seal unit is properly assembled and aligned to the correct tolerances;
- there is no lateral movement or vibration of the shaft. Worn bearings in a pump or an unbalanced impeller in a pump or agitator will usually be attended by seal problems.

As a single mechanical seal holds its seal with the assistance of the pressure of the pumped fluid, leaks normally develop slowly. A failure of the seal fluid to a double mechanical seal assembly can lead rapidly to a high rate of leakage from the inner seal.

For more specialist duties where leakage cannot be tolerated, pumps are available without seals. Types available and in general use are:

- magnetic drive centrifugal pumps. There is a possibility of overheating and catastrophic failure if there is a blockage solids or if there is a loss of flow;
- 'canned' centrifugal pumps in which the rotating part of the drive motor is sealed inside the fluid container. Because the pumped fluid lubricates the impeller bearings, these pumps cannot be used if the fluid does not have the necessary lubricating properties. As with magnetic drive pumps, canned pumps are also vulnerable to overheating and failure on loss of flow;
- diaphragm pumps. These are reciprocating pumps in which the movement of the shaft is transmitted to the fluid by a flexible diaphragm which also seals in the fluid. These pumps are often used as metering devices and can be fitted with multiple heads for the supply of several fluids. The flowrate is varied by changing the stroke of the drive.

shaft and the system is readily combined with the overall control system of the process. These pumps are of particular value for use in applications where the flowrate required is too low to allow more conventional metering devices to be used.

### 5.2.6 Gas compressors

Compressors perform the same function for gases as pumps do for liquids, namely to increase pressure so that fluids can be transported through the plant. In the same way as pumps, they are driven by rotating or reciprocating shafts and the sealing arrangements are similar. An important difference is that the lubricating and cooling requirements of the interface between the moving and the stationary part of the seal installation are more difficult to organise with gases. The common types of seal used are:

- labyrinth, which consists of two sets of interlocking teeth, one rotating, one stationary;
- restrictive ring, comprising multiple stationary carbon rings in place of gland packing;
- mechanical seals similar to those used in pumps;
- liquid film in which liquid is injected into the space between two sets of close tolerance bushes.

It is usual for there to be a gas bleed through the shaft sealing system and this will constitute one of the process gas releases whose fate should be assessed.

### 5.2.7 Agitator Systems

The standard method of agitating the contents of a reactor vessel is the use of a rotating impeller. The main environmental issue associated with the use of agitator systems is the seal that can be achieved at the point where the agitator penetrates the reactor. If the seal is poor significant emissions may arise.

The sealing methods used for pumps are also used for reactor agitators with the difference that the difficulties of suppressing lateral movements of the shaft are amplified. Steady bearings at the lower end of the agitator shaft are sometimes used but, immersed in the process fluid, lubrication can give difficulties. Nevertheless, as with pumps, the double mechanical seal is the most commonly used sealing mechanism for agitators. Lip seals and inverted cup seals are sometimes used but these are only of use for pressures of up to a few inches water gauge.

Other methods of achieving mixing without seal problems are:

- jet mixing as part of a pump around system;
- static mixers.

These methods are often used in conjunction with the addition of reactants if reaction is very rapid and it is important for the reactant to be diluted rapidly or if the mixture has to be cooled immediately to prevent runaway. Other methods include:

- vibrating as opposed to rotating mixers;

- gas sparging This is a cheap, no moving parts system with a great potential for stripping volatile material into the overheads system where it may need to be recovered, recycled or treated.

As with a consideration of pumps, compressors etc. the choice of agitator will be entirely process specific.

## 5.2.8 Valves

Valves constitute one of the most frequently used items of equipment in a process plant. Even a relatively simple manufacturing installation will contain several hundred valves. Valves are used for two purposes in a plant: either to control the flow of fluid (gas or liquid) through a pipe or to provide the facility to stop flow when required.

There are many different methods of introducing an obstacle to flow to meet the specific requirements of an application. The most common forms are:

- the gate valve which inserts a flat sliding plate across the flow;
- the globe valve in which a disc is lowered onto the flow orifice;
- plug or ball valves which use a rotating plug through which a lateral hole allows flow to pass - or not when the aperture is rotated away from the flow.

All valves can present environmental consequences if they fail in their primary purpose of isolation. Valves which pass material when closed can cause cross-contamination of material during processing or leakage of material to the environment. It is for this reason that it is usual to make extensive use of "double block and bleed" arrangements in conjunction with blank flanges and slip plates to secure positive isolations as far as possible.

The operating stem of the valve is usually sealed by a packed gland in a similar arrangement to that used in a pump gland packing. As with pumps, the effectiveness of the seal can depend on the level of inspection and maintenance. The difference is that valves generally receive even less attention than pumps.

A number of designs of valve are available in which the actuating devices are isolated from the process fluids either by bellows arrangements or by the use of flexible diaphragms. These valves do not leak to atmosphere in normal use but on failure, leakage rates can be high.

Most of the minutiae of valve design, choice and sealing is primarily the concern of the plant operator. The Inspector would seek only to establish that the operator was aware of the potential problems; that the relevance of these aspects of design to the environment had been considered and that if the risk of environmental damage could be high that a management programme would be in place to control these risks. It will be appreciated that many valve related safety and environmental incidents have been caused not by mechanical failures but by failure to ensure that valves were closed or locked closed. Management operating procedures can therefore be as important as the choice of equipment.

### 5.2.9 Purging

Plant will normally require purging with air after shut down or after campaigns if vessels are to be opened or if entry to equipment is required. Similarly, on start up, air is displaced from the system by inert gas (usually carbon dioxide or nitrogen) to ensure that a flammable atmosphere does not form when organic material is introduced to the system.

The purging system should be the result of formal design modified by plant experiment and analysis. Attention should be paid to ensuring that potential 'dead spots' are purged. Concentration limits for the purging procedures will be chosen by reference to the flammability limits of the material in the system with the application of suitable safety factors. Continuous analysis of the oxygen content of the purge gas can sometimes be useful in order to minimise the quantity of purge gas used.

Purging can be done continuously using a once through flow or by raising the pressure of the system with purge gas and then releasing the purge. Pressure purging is essentially a system of purging by mixing; continuous purging, a process of displacement. The relative advantages depend on the geometry of the system. pressure purging will impose greater instantaneous loads on abatement equipment.

### 5.2.10 Heating and cooling

In all the heating and cooling applications there is a potential for coolant, cooling water, heat transfer medium or steam to leak into the process stream, or, conversely for process material to leak into the heating/cooling system. Steam pressures are usually too high for there to be leakage into the steam system. If a plant is handling corrosive materials and there is a history of corrosion failure a regime would be expected which used:

- corrosion monitoring techniques at critical points;
- a leak detection system to reduce organic losses through vaporisation or purges from the cooling system.

## 5.3 Reaction Stage

Agitated vessel reactors are extensively used in the sector covered by this study because:

- many chemical steps can be achieved using the same reactor;
- modern computer control methods allow precise and reproducible conditions to be imposed on each batch. Computer control can also be used to control the valve sequencing to make the operation more secure. Computer software can, however, introduce additional hazards so that a number of manual and mechanical safeguards must be left in place.

Typical reactor sizes vary between 2 m<sup>3</sup> and 50 m<sup>3</sup> (20 m<sup>3</sup> will provide one road tanker load). More specialised reactions such as chlorination and nitration might use reactor designs specifically designed for the purpose.

### 5.3.1 Fundamental Design Points

Many processes were designed under very different cost and environmental constraints from those which apply today. It is valuable to consider what features of the design chemistry and engineering contribute to downstream problems and to consider which factors could be changed. Thus the operator may consider whether the following issues can be practicably addressed:

1. What impurities in the inlet feeds contribute to purification problems later in the process?
2. What side reactions are reducing yields?
3. Could the process reactants, catalysts, temperatures or pressures be changed to improve performance?
4. Does the reaction require a solvent and is this solvent appropriate?
5. Is a catalyst used? Could its removal be more easily achieved?
6. Is the order in which reactants are added optimal for limiting losses?
7. Can the use of relief devices be eliminated by designing the reaction vessel for a suitably high pressure, or by adopting a high integrity instrumentation and trip system?
8. Can reaction yields be improved by better quality control of raw materials and the use of more sophisticated computer control of the reaction system?
9. Are sample lines as short as practicable and ensure that unwanted sample material is returned to the process?
10. Can off specification product be retained and reworked to recover useful materials?
11. The reaction and purification areas of the process will receive the most frequent drainings, spillages, leakages and other contaminants. Thus can the floor area be made impermeable, chemically resistant and limited in area by kerbing so as to drain to the process effluent system?
12. Have Hazop studies been used to limit the problems of choked lines associated with the use or production of high melting point material?
13. Would small scale continuous reaction technology be feasible and more appropriate?
14. Could novel reaction techniques such as biological methods, supercritical operation, electrical or radiation induced reactions be used and if so does the operator fully understand the environmental implications of their use?

### 5.3.2 Liquids

Much production in this sector operates in campaigns wherein different products are made in each successive campaign. At the end of each batch and campaign it is important to remove as

much of the preceding batch as possible. There are many features which will both assist this process and also limit the loss of material to drain. For example, the following issues may merit consideration:

### **Reactor system design**

- minimise use of internals such as baffles and coils in the reactor;
- use smooth reactor walls to eliminate crevices;
- fit a flush bottom outlet to the reactor;
- design associated piping to slope back to the reactor or to a drain point for liquid recovery;
- ensure sufficient headroom under the reactor to allow collection of rundown in drums if necessary;
- minimise pipe runs and extraneous branches for instruments, sampling lines and cross connections.

### **Operational methods**

- design or modify pipework to allow air or nitrogen blowing;
- design or modify pipework to allow the use of pigs to clean lines. This is only practicable on larger diameter and longer lines;
- ensure that the system is kept as warm as practicable during emptying in order to facilitate run down;
- endeavour to sequence campaigns so that cleaning between campaigns is not required. This may be possible if the next campaign is to manufacture a similar product with only a small variation in formulation. It will not normally be possible in the manufacture of pharmaceutical or other high quality products;
- if a complete clean is necessary then:
  - consider the use of a solvent which can be used subsequently or can be collected for recovery of solvent and product.
  - use cleaning methods which minimise the use of the cleaning agent. Some of the widely practised methods of achieving this are the use of steam cleaning or the use of rotating spray jets or spray balls. The performance of spray balls and rotating jets can be enhanced by using high pressure cleaning systems.

### 5.3.3 Vapours

In general terms the overhead system of a reactor will probably need to handle:

- the consequences of emergency conditions;
- vapours displaced during the charging of reactants;
- material vaporised as a consequence of the heat evolved in the reaction;
- material vaporised in order to remove products and wastes from the reactor;
- material entrained with inert gases in the system.

The amount of vaporisation occurring during the charging of vessels can be reduced by avoiding splash filling and using bottom filling instead. This also reduces the risks of explosion from static electricity generation and discharge.

Local treatment of the vapour discharges from a reactor system will often be installed in addition to, or independent from, a plant emission abatement system in order to achieve direct recovery of material. The most common operations for this purpose are condensation and absorption.

On existing plant, the equipment may well have been designed to meet financial or safety constraints rather than environmental criteria and scope can therefore exist for improved environmental performance. Opportunities might exist to enhance the performance of the equipment by increasing the heat transfer area, changing the packing in absorption towers, chilling the heat transfer medium or changing the absorbent. The key operating variables of the systems should be defined and controlled.

## 5.4 Separation Stage

On completion of the reaction it is usually necessary to separate the desired product from the other components in the reaction system. These can be unreacted feed, by-products, solvents added to facilitate the reaction, catalysts etc. Sometimes the initial separation can be achieved within the reaction vessel; more often the reactor contents are pumped to other equipment for separation.

A full description of the equipment available to achieve these separations is outside of the scope of this study. Standard chemical engineering texts provide full details of the types of equipment, their construction and mode of operation.

These separation procedures have a potential for environmental impact because:

- complete separation is rarely achieved. There will be, practically always, some loss of the desired product with the reject stream;
- many separations introduce additional materials to the process, most usually as solvents or wash water, which ultimately require recovery or disposal.

### 5.4.1 Liquid - Vapour Separations

The most widely used liquid-vapour separation techniques are:

- evaporation;
- steam or gas stripping;
- distillation.

Many of the comments applying to the overhead systems of reactors are equally applicable to these techniques.

The vapours will normally be condensed and sometimes a proportion will be returned as reflux to a contacting column. Any mass transfer contacting device will have been designed for liquid and gas flows to produce a suitable contacting surface area. If the design conditions are not adhered to effective operation will not result. This applies to flows which are too low, or too high or the wrong ratio. A useful diagnostic tool may often be the checking of the heat balance by monitoring flows and temperature differentials.

Contaminants can cause excessive foaming and excess inert gas can limit the condensation achievable. Equally, failure of the flow of cooling medium to the condensing system will stop condensation and may result in overpressure or release of pollutants to the atmosphere. Instrumentation needs to be in place to warn of faults in the system.

### 5.4.2 Liquid-Liquid Separations

The most widely used liquid-liquid separation techniques are:

- extraction with water or solvent;
- decantation;
- centrifuging;
- multi-stage contacting.

Solvent extraction can be a very effective, low energy method of separation. The process requires, first, the dispersion of one immiscible phase within the other to promote mass transfer across the droplet boundaries, followed by as complete a separation as possible of the two phases.

The mechanics of both the dispersion and the coalescence are heavily influenced by the surface properties of the fluids. These properties can be changed markedly by small quantities of surfactant material such as dust particles which can cause emulsions to stabilise or inhibit coalescence. Even with good separation there is usually a secondary haze which can result in up to one percent of material going with the wrong phase.

In batch operations, a more commonplace problem is the detection of the interface while a separation is being done by hand. A 'deadman's handle' device can be used to ensure that the operator remains in attendance, although these can be defeated. A number of instrumentation devices are available such as capacitance probes, conductivity meters or even diversion vessels to collect interfacial material. Operators should consider whether instrumentation is a practicable solution for improving separation.



Ion exchange, as its name implies, is effective for removing ionic material such as dissolved metal which has been used as a catalyst in the process. Ion exchange resins are available which can operate in organic liquids without undue swelling, but the regeneration sequence still requires the use of inorganic acids or alkalis.

The whole regeneration sequence is often complex and the possibility of axial back mixing producing mixed effluents for disposal should be considered. The operator should be able to demonstrate that all of the possible consequences of less than ideal operation have been catered for.

### 5.4.3 Solid - Liquid

The main solid-liquid techniques are:

- centrifuging;
- filtration;
- sedimentation and clarification;
- drying;
- crystallisation.

All of the solids produced from a solid-liquid separation are wet with the mother liquor whence they were separated, so most of the equipment used incorporates washing stages to produce a further stream to be processed. Many filtration machines use added solid filter aid to improve filtration which adds to the solid disposal load. All of the devices are subject to failure caused by solids breakthrough so that it would be expected that all will have instrumentation to detect malfunction. Additional 'guard' filters of small capacity are often installed downstream as a protection against breakthrough.

If the liquid phase is the reject stream and the solid is to be reprocessed to make product, further processing is also required for the liquid to allow recycling or recovery of useful material. The wash liquid will have been chosen to be compatible with the next phase of the solid processing and this stream may constitute a second stream for reprocessing.

If the solid phase is the reject stream and the liquid goes forward to product, two stage washing might be used, one to ensure product recovery, the second to remove the liquor of the first wash. The solid will then be removed, perhaps by backwashing to produce a residual stream for which options of recycle, recovery or safe disposal will have been considered.

Poor procedures and practices in the cycle of separation, flushing, washing and restarting can result in escapes of volatiles to atmosphere or the production of large quantities of weak effluents. An inspector might require a full rationale of the procedure chosen with supporting evidence of the control mechanisms in place.

Drying is most usually associated with final purification and preparation for packaging. A more effective separation to much reduced moisture levels, perhaps by the use of a vacuum, might result in much improved economic and environmental performance at the purification stage of the process.

## 5.5 Purification Stage

At the purification stage the part treated product stream is separated from the accompanying contaminants to produce the final product compound. The range of unit operations and the equipment employed to perform them is similar to that employed in the separation stage. As with separation equipment, a detailed description of the full range of types of equipment is available in standard chemical engineering texts, but lies outside the scope of this report. The emphasis of the design philosophy is, however, different.

Frequently, at this stage, the purge is made of the co-produced wastes from the process. In the past, the disposal of waste, either to atmosphere or to drain, has not been of economic significance so that the design ethos has been to achieve the highest purity of product for the lowest capital and revenue cost. Often, the higher the value of the product, the less would have been the concern for the rejected waste.

Purge streams such as distillation bottom product, filtrates or centrifugates, wash liquors or mother liquors from crystallisation processes have been rejected in the past as having no economic value. It may be appropriate to consider how these streams can be re-examined with a view to determining the potential for extracting material for recycle to the process or reuse in some other process.

On older plants, or plants designed to an earlier philosophy, there is often scope for reducing releases. These measures will either reduce the impact of the releases or reduce the costs of downstream abatement. Any serious attempt to reduce the releases at the end of a process will start with an examination of the sources of the material being purged. There are three main sources:

1. Impurities in the raw materials. A change in the specification of raw material might remove a considerable abatement problem.
2. Material introduced into a process. Suppression of leaks (or ingress of air), or changing of solvents or catalysts might improve the waste situation.
3. A change in reaction conditions could improve the selectivity of the reaction and reduce by-product formation.

### 5.5.1 Liquid Products

Liquid products are usually refined by distillation. Sources of loss are:

- entraining gas - There will often be some gaseous release of inert gases from the system or light material formed in the reactions. These off gases will carry further volatile material either as vapour or as entrained droplets or mists. Supplementary condensing areas or the use of a cooler heat exchange fluid can improve the recovery rate. Coalescing demisters are relatively cheap and easy to install;
- ineffective recovery - A better split within the distillation column can be achieved by using more extraction stages or more reflux. This would normally imply a considerable capital expenditure but the use of more modern packing or high

efficiency trays can often produce a marked improvement for a modest capital investment. In a batch distillation the degree of separation can be influenced similarly with the added flexibility of being able to allow more time for the separation. Running a column on total reflux before beginning product takeoff may allow the yield to be improved on some occasions;

- filtration - Enclosed filtration is usually used and this is not normally a source of great loss. Liquid discharge to clean or to change filters should be returned to the process.

### **5.5.2 Solid products**

The final stages of the preparation of solid products will usually consist of the separation of the solids from the mother liquor followed by washing and drying. Frequently a further stage of dissolving and crystallisation is required to produce the desired quality. Washing and crystallising activities have the potential to produce large volumes of dilute liquors from which the recovery of anything useful is difficult and whose treatment can also be costly.

As far as possible arrangements should be made to install a countercurrent system of operation, either by imposing continuous operation of that section of the plant, or by installing more holding vessels to allow the countercurrent principle to be used. The same principle of endeavouring to achieve countercurrent operation applies to drying.

The option of storing the drying gas is not available, but if countercurrent operation cannot be achieved measures can be taken to ensure that if solvent is being removed, the first flow of drying gas can be limited to ensure a maximum concentration of solvent which can be recovered by condensation.

## **5.6 Design of a new process**

The important environmental feature of a new project for chemical manufacture is that environmental issues are an integral part of design discussion at every stage of the design, beginning with the initial concepts.

Ultimately every release from the process should be considered as another product whose quantity and quality are measured, controlled and recorded. This list should include releases generated from flushing and cleaning operations. For final release to the environment the releases will probably require treatment and the costs of these treatments will form part of the financial modelling of the process.

At the initial stage of the development of the process there should be a formal and exhaustive review of:

- all raw materials;
- all intermediates;
- products;
- planned releases;
- possible unplanned releases such as:

- spillage;
- pressure relief;
- shut-down/start up relief;
- off-spec products.

The objective is to assess the possible environmental impacts of these materials in order to develop a strategy for minimisation, containment and treatment. Particular attention may have to be paid to the selection and management of solvents. The ETBPP has brought out guidance on solvent management (ETBPP 1996a).

The process should then be reviewed to consider what changes can be made to reduce the impacts and the quantities of the releases.

Considerations raised at this point might include:

- improving the selectivity of the reaction;
- investigating means of reducing deposition in equipment;
- changing solvents to more readily recoverable or treatable materials;
- improving raw material quality;
- improving the efficiency of specified separations in the process;
- reducing the total inventory of the processing units, perhaps by intensification of operations.

The quality and effectiveness of a review at this stage depends upon the calibre and the commitment of the members of the team engaged in the review. Members should be drawn from the designers in process engineering departments and the operating managers who will run the process. The USEPA has brought out guidance for process operators on how they should assess the environmental impacts of the equipment they use (USEPA 1997).

HAZOPs are now widely applied throughout the chemical industry but the use of studies at several stages in the development of a project has not been quite as widely adopted and the use of the techniques to question the basic premise of a process is not general. Nor is it, as yet, general to pose fundamental questions about environmental impact. BP and Costain Oil have developed an Environmental Optimisation (ENVOP)<sup>®</sup> technique that seeks to introduce environmental considerations into HAZOPs, in particular by setting environmental objectives, using different keywords and undertaking technical and economic analysis (Potter 1993).

HAZOP techniques should be adopted for this first process review and it is vital that environmental specialists are key members of the team. A key purpose of the review is the production of a preliminary environmental impact assessment.

Processes are often developed to an advanced state within research laboratories before moving to the project stage. Others are imported from another branch of the company or a licensor in another part of the world. In these cases a profound environmental review will probably not have been conducted. It is important that the review should be done as soon as possible and the awkward issues confronted in spite of the difficulties of time and politics which emerge. Typical features which can be found to have been overlooked include (among many others):

- failure to check that laboratory simulations have used exactly the same feedstock from the same source as is proposed for the plant;
- incomplete assessment of the effect of the build up of contaminants in recycle streams leading to unexpected purges;
- incomplete arrangements for corrosion monitoring;
- failure to conduct adequate treatability trials of emissions and effluents.

Inspectors would not be involved in the details of the development of a design concept. The Inspector would, however, wish to be convinced that such environmental reviews had been done before expenditure began. Assurance would also be sought that the concept of reducing the releases to the minimum had been investigated and the costs reviewed before the design was frozen.

Details of constructional design principles are dealt with in other parts of the report. The essential concepts can be summarised:

- **identify and characterise all releases;**
- **segregate all releases at source** and maintain them separate for as long as possible. This allows measurement and diagnosis; it also retains the flexibility to pursue waste minimisation and treatment schemes in the future;
- **treat at source whenever possible.** This can often be a cheaper option as many of the segregated streams are more concentrated, lower volume and less complex mixtures than the combined flow;
- **ensure containment.** It is important to ensure that all spillages are contained and directed to the effluent system and that the effluent system itself does not leak and contaminate the land or groundwater. Specification or equipment should take into account the likelihood of fugitive emissions, the positioning of piping and of vessels containing environmentally significant streams should allow rapid detection and rectification of leaks;
- **provision for flow equalisation and for emergencies.** If treatment is on site the design must be capable of dealing with fluctuations in flow, composition and concentration. For effluents this translates into the provision of holding and balancing tanks and sometimes for emergency storage to cope with unusual events such as firefighting. On small sites it is not unusual for the total effluent flow to be held in intermediate storage until cleared by analysis for release.
- **reliability.** If on site treatments are installed, their operation will be implicit in the site authorisation. Any failure in the treatment units is as important as the site power supply for it can also provoke a plant shut down.

## 5.7 Conclusions

As the scope for further end-of-pipe reductions in releases becomes both economically and technically more difficult to achieve it has to be recognised that the prevention and

minimisation of pollution within the process is a key element of the future evolution of the IPC system.

However, it is not the intention of the IPC system to involve inspectors in the detailed design of processes. This activity is best left to process operator and their contractors. Indeed such is the sheer number of variations in process techniques that may be applied at one site but not another that even if it was desirable to issue detailed guidance on process techniques it would probably not be feasible.

Despite these caveats inspectors can still take an informed position on the process techniques applied by a process operator. In particular, an inspector should seek to ensure that:

- process operators have identified all environmental effects associated with their process techniques;
- prioritised these effects for control; and
- implemented management, operational and maintenance programmes to ensure that the most important effects are prevented or minimised.

## **6. AIR ABATEMENT TECHNIQUES**

A wide variety of techniques are available for the control of releases to air. The abatement of releases of volatile organic compounds (VOCs) is the primary concern for this sector and this is discussed in Section 6.1. Section 6.2 addresses the abatement of releases of particulates.

### **6.1 Volatile organic compounds (VOCs)**

#### **6.1.1 Introduction**

Releases of VOCs may be broadly characterised as those from:

- fugitive sources (leaking valves, pumps etc.); and
- point sources (reactor, separator release points etc. as well as situations where fugitive emissions are collected and sent for point abatement).

Techniques for the abatement of the former are process related and are discussed in Section 5 of this report. The control of VOCs from point sources is an issue for many other IPC sectors but the main factors that differentiate this sector in terms of the abatement techniques that can be applied are the:

- intermittent nature of releases from batch processes; and
- complex nature of the gas streams involved, with many VOCs often being present as well as moisture, particulates, combustion by-products and acid gases.

Both of these issues have a profound influence on the selection of abatement techniques. The Agency has already issued considerable guidance on abatement techniques for dealing with:

- particulates - Technical Guidance Note (Abatement) A3 (HMSO 1994a);
- acid gases - Technical Guidance Note (Abatement) A3;
- combustion by-products - IPC Guidance Notes on Combustion Processes (S2 1.01) (HMSO 1995b) and Incineration (S2 5.01) (HMSO 1996b); respectively.

These documents should be referred to where these pollutants are of relevance. This guidance note concentrates on identifying what implications these additional pollutants may have for the selection of the optimum VOC abatement technique.

Techniques for the abatement of VOCs may be broadly characterised as those that:

- recover the VOC and offer the potential for recycle/reuse; and
- destroy the VOC.

It is important to note that unless a viable recycle/reuse route is available for the former techniques then there will still be a need for disposal, whether it be on or off-site.

There are three types of VOC recovery technique that offer the potential for recycling/reuse. These are:

- adsorption;
- absorption; and
- condensation.

The two main types of destructive technique for abating VOCs are:

- thermal oxidation; and
- biological oxidation.

All five of these techniques have been and will continue to be widely applied in the sector. There are many different variations on each of them and these are discussed in more detail below. In a number of situations, technical constraints may mean that only one type of technique is viable for dealing with a gas stream, whilst in others a number of options may merit consideration. Plasma, polymer membrane and corona based techniques are being developed but have yet to be demonstrated on an industrial basis. They are discussed further in Chapter 9.

The complexity of the gas streams generated by this sector mean that it is often necessary to combine together two or more types of technique. Such combinations may include (Mycock 1995):

- pre-treatment to remove moisture, particulates etc. prior to the main abatement stage;
- concentration of a dilute gas stream to make the application of a high performance abatement technique possible;
- a primary removal stage to reduce high concentrations, followed by a 'polishing' stage to achieve low release levels.

The use of combinations has cost implications as the size and complexity of the abatement system is increased but this may be the only way of dealing with a particular problem. In such instances it is particularly important that the operator:

- considers in-process changes that make a single treatment step viable; and where this is not possible;
- robustly characterises the gas stream(s) involved and identifies the constituents that may require differential abatement.

The decision as to whether to apply recovery or destructive techniques is a complex one. The feasibility of using the former will be greatly enhanced if the recovered VOCs can then be recycled/reused. This issue is discussed below, followed by a commentary on the application of the five techniques in the sector.

Guidance has been issued in Germany on the use of VOC abatement techniques (VDI 1981, 1990, 1991, 1995, 1996a/b and 1997) but this tends to be less useful than that issued in the UK and USA and has proved to be of limited use in this study.



## 6.1.2 Characterisation of releases

Before selecting the appropriate technique(s) it is important to systematically quantify flows, chemical compounds and concentrations over all potential operating conditions. This is particularly important for batch operations where there may be rapid changes in all of these factors. Quantification allows opportunities for in-process minimisation to be considered as well as aiding in the selection of the appropriate abatement techniques. Particular attention may have to be given to vent header systems that receive gas streams from a number of different sources. Consideration should be given to the potential interactions between these gas streams in the header system.

Chadha (1993) summarises the main causes of releases to air from batch operations as follows:

- introduction of air (oxygen) into reactors for oxidation of reagents;
- introduction of air to the reactor during reagent charging;
- leakage of air into process equipment;
- use of liquid nitrogen or dry ice to provide direct-contact cooling;
- use of nitrogen or other non-condensable to transfer volatiles or for blowing lines;
- use of nitrogen for breaking vacuum or providing an inert atmosphere;
- generation of non-condensable gases (such as CO<sub>2</sub> or hydrogen) as a product or by-product of a reaction;
- generation of VOCs with vapour pressures greater than atmospheric pressure at process temperatures as a product or by-product of reaction;
- evacuation of vessels containing VOCs e.g venting a vessel to vacuum equipment to reduce its operating pressure;
- heating of vessels containing VOCs so as to cause expansion and increase in organic vapour pressures;
- stripping of VOCs during vacuum distillation;
- boiling of pure solvents in vessels to clean them between batches or campaigns.

These are just some examples of the sources of releases from a process and an inspector could expect that a process operator has identified and prioritised releases from their process. Process techniques outlined in Section 5 could then be applied to reduce releases at source.

Li (1995) has also summarised the US approach to developing an emissions inventory for a process as follows:

- decide methods to determine emission rates. These may include:
  - stack testing and monitoring, which whilst generally the most accurate method is also the most expensive and time consuming;
  - emission factors have been compiled by the USEPA (1991) under its AP42 programme. As yet AP42 does not appear to contain factors that would be of use to this sector;
  - material balances are probably the cheapest approach but also the most inaccurate;

- engineering equations are perhaps the best compromise between the accuracy but high cost of stack testing/monitoring and the cheapness but inaccuracy of material balances (USEPA 1994b);
- identify emission sources, see also Chadha 1993. It may be possible to use the step by step process operating instructions to breakdown the process into sources of releases to air
- gather data. The approach adopted should be based on a prioritisation of potential releases, with most effort being attributed to the main sources. The chosen method(s) for determining emissions can then be applied;
- manage data. It is possible that large amounts of data will be gathered and it is important that a systematic approach is taken to handling and storing it;
- present results. Again the results of any data manipulation should be presented in a clear and logical manner with clear attribution to process units.

### 6.1.3 Recovery versus destruction for VOCs

Recovery followed by reuse/recycling is generally preferable compared to destruction. Recovery should therefore be maximised at all stages in the process. A number of issues need to be considered when deciding if recovery is a viable option. These include:

- **the composition of the gas stream.** Generally the more complex the mixture of compounds present, the harder recovery will be to justify technically or economically. Recovery is particularly amenable for gas streams containing a single component or streams containing a small number of components that can easily be separated from each other after initial recovery;
- **quality requirements.** Even if recovery is technically and economically feasible it may not be possible to recover the target VOC with a quality sufficient to satisfy the requirements of the process. Under certain circumstances minimum quality requirements will be specified by the customer or another regulatory body, in particular for the manufacture of pharmaceuticals. It may be possible to identify an external market for the recovered VOC but there needs to be a certain degree of confidence about the long term viability of such markets to justify investment;
- **economics.** The economics of recovery will reflect the complexities associated with the gas stream's composition and the quality requirements of the process as well as such considerations as the unit cost of the VOC and the volume that can be recovered. Thus for very high cost solvents such as THF, high cost recovery techniques may be a viable option;
- **release levels.** In certain situations recovery techniques may not provide sufficiently good release levels to be justified as the preferred technique.

## 6.1.4 Adsorption

Adsorption is the process by which pollutants (the adsorbate) are removed from a waste stream by adhering to the surface of a solid material (adsorbent). This solid material usually has an extensive internal pore structure to maximise the surface area to which the pollutant can adsorb.

The adsorbent has a finite number of points to which pollutants can adsorb and therefore needs to be periodically regenerated (cleaned) to purge the adsorbent of pollutant. Without this regeneration step the adsorbent would become saturated and with no available adsorption points left on the bed the pollutant would pass through unabated, this is often known as 'breakthrough'. It is the regeneration step that provides the opportunity for the pollutant to be recovered and recycled. If only recovery, but not recycling, is feasible then the pollutant will need to be disposed of.

Of all the techniques considered in this section, adsorption is perhaps the least flexible in terms of the gas stream to be controlled. This sensitivity is reflected in the following factors, all of which may influence the viability of utilising adsorption:

- system for holding the adsorbent;
- type of adsorbent used;
- chemical characteristics of the gas stream;
- physical characteristics of the gas stream.
- re-generation method used.

Each of these factors is discussed in turn below:

### Arrangement of adsorption system

There are five basic ways of supporting the adsorbent in adsorption systems. The first two are not generally amenable to recycling/reuse and as such give rise to a, usually off-site, disposal problem. The latter can be used for recycling/reuse but if this is not viable then there will be a requirement for a further disposal step. The five systems are:

1. **Canister capture systems** are the simplest of the systems, usually consisting of a canister containing an adsorbent. They can be fitted easily and cheaply to sources of low flow emissions, Mycock (1995) suggests that they are most amenable for concentrations below 1 ppm and the USEPA (1995) suggests a maximum flow of 170 m<sup>3</sup>/hr, where the composition of the gas stream is relatively homogenous, for example, from storage tanks. Because of their small size they take up little space and thus are particularly useful for older processes where size and economic constraints may preclude the fitting of a larger system. The installation and removal of such systems is usually undertaken by the supplier.

Despite their relative simplicity and ease of use there may be BPEO considerations associated with the disposal of a large number of spent capture canisters. Spent canisters are rarely if ever regenerated. This reflects the considerable costs associated with analysing each individual canister when returned to the supplier and the high costs of

regenerating a large number of small units. Larger fixed bed units, see below, provide sufficient economy of scale to justify this cost.

When using this technique the operator should have in place a system which anticipates or detects breakthrough in the system. An anticipatory approach ensures that systems are replaced at fixed intervals, intervals which are less than the expected time to exhaust the canister's adsorption capacity. Alternatively, regular checks on the exhaust gas composition could be undertaken to detect when the system is fully adsorbed and the VOC is passing through the system unabated. The exact approach adopted will depend upon any odour or toxicity problems associated with the VOCs present. It may be appropriate to adopt a dual approach whereby no monitoring is undertaken until, say, it has been calculated that 80% of the drum's capacity has been utilised.

2. **Skid mounted capture systems** are a variation on the canister based system. Although larger than canister systems (typically containing 1000 kg of activated carbon compared to 75 kg in a canister) they are still mobile and can be retro-fitted with relative ease to existing processes for however long may be required. They are more expensive to install than canister systems but have a larger adsorption capacity and thus may be more cost effective in the long run. Skid mounted systems are usually returned to the supplier for regeneration, typically under a leasing contract;
3. **Fixed bed systems** are probably the most widely used in the chemical industry. They usually consist of two or more fixed adsorption beds. At any given time, one bed will be operating on-line as the pollution abatement technique, whilst another bed will be being regenerated. On completion of their respective cycles their mode of operation is swapped.

Variations on this basic two bed approach include the use of three beds, where one bed is kept permanently on standby in case one of the primary beds should fail. In a few cases, for example where the time taken to saturate a bed is very much shorter than the time taken to regenerate a bed, further beds may be utilised. Certain batch operations which are only used infrequently may find it to be possible to operate with only one bed but the reduced flexibility that this affords should be borne in mind.

4. **Fluidised beds** are a variation on the fixed bed system and use a fluidised rather than solid bed of adsorbent. Fluidised beds tend to be more complex than fixed bed systems but at the same time their smaller size may reduce the capital costs. The main problem with fluidised beds is the relatively high attrition rate on the activated carbon that results in the need for frequent 'topping' up (Mycock 1995). Attrition may also result in the entrainment of particulates in the exhaust gas stream.
5. **Continuous adsorption-desorption** is not widely used in this sector, being generally more complex and expensive to operate and thus more appropriately applied to continuous operations. Such systems may consist of a large, slowly rotating (approximately 1-2 revolutions per hour) drum of adsorbent. The drum passes through three discrete areas as it rotates, an adsorption area where it is impacted by the gas stream, a desorption area and a drying/cooling area.

Alternatively clean adsorbent may be fed continuously into the top of a column and be passed downwards on a series of trays. The contaminated gas stream enters the bottom of the column and is passed upwards through the descending adsorbent. As the adsorbent passes down through the bed it strips the pollutant(s) from the gas stream. On reaching the bottom of the bed the saturated adsorbent is removed and passed through a regeneration column (usually using inert gas or steam). After passing through the regeneration column the clean adsorbent is fed into the top of the bed once again. Physical wear and tear usually requires a constant feed of new adsorbent and there is a risk that adsorbent in particulate form may be vented in the exhaust gas from the system.

## Adsorbent

There are wide range of adsorbents available. The main ones, together with some of their operational strengths and weaknesses, are summarised in Table 6.1 (Mycock 1995, ETBPP 1996b, HMSO 1994b).

**Table 6.1 Main adsorbents**

Adsorbent	Strengths	Weaknesses
granular activated carbon (GAC);	<ul style="list-style-type: none"> <li>• good for non-polar compounds i.e many VOCs</li> <li>• extensive experience of their application in a wide range of situations;</li> <li>• wide range of grades available at different costs to deal with a range of operating conditions, VOCs and desired release levels</li> </ul>	<ul style="list-style-type: none"> <li>• poor for polar compounds</li> <li>• poor for high VOC concentrations (above 10000 ppm, although dilution can be used to reduce the inlet concentration);</li> <li>• poor for very high or low molecular masses (only effective in the range 45-130);</li> <li>• poor for mixtures of high and low boiling point VOCs (the former will tend to be preferentially adsorbed at the expense of the latter)</li> <li>• poor for relative humidities above 50%</li> <li>• poor for reactive compounds (organic acids, aldehydes, ketones and monomers)</li> <li>• poor for high boiling point compounds (plasticizers, resins, long chain hydrocarbons (C14 and above), phenols, glycols and amines)</li> </ul>
activated carbon mat	<ul style="list-style-type: none"> <li>• can be used for the removal of VOCs;</li> <li>• compared to GAC they have a relatively large number of adsorption points per unit volume, which reduces the number of regenerations required</li> </ul>	<ul style="list-style-type: none"> <li>• as for GAC</li> <li>• up to one hundred times more expensive than GAC</li> </ul>

macroporous polymer particles;	<ul style="list-style-type: none"> <li>• can be used for the removal of VOCs</li> <li>• good for continuous adsorption/desorption processes</li> <li>• durable;</li> <li>• unaffected by high humidity</li> <li>• does not catalyse degradation of unstable VOCs;</li> <li>• high purity VOCs recovered</li> </ul>	<ul style="list-style-type: none"> <li>• ten times more expensive than GAC;</li> <li>• cannot be used for very polar compounds</li> <li>• cannot be used for low boiling compounds</li> </ul>
molecular sieve zeolites;	<ul style="list-style-type: none"> <li>• can be used for the removal of VOCs, although it is not widely applied for this purpose</li> <li>• good for dehydrating gas streams</li> <li>• hydrophobic zeolites are available which have a higher capacity than GAC at low VOC inlet concentrations and a higher capacity at high relative humidities (above 50%)</li> <li>• non-flammable, therefore good with VOCs that may present a fire risk</li> <li>• uniform size of pores means this approach can be used to separate compounds on the basis of molecular mass and shape</li> </ul>	<ul style="list-style-type: none"> <li>• expensive</li> <li>• if de-hydration is not desired, can preferentially adsorb water and allow pollutant to pass through</li> </ul>
silica gel;	<ul style="list-style-type: none"> <li>• good for dehydrating gas streams</li> </ul>	<ul style="list-style-type: none"> <li>• generally not effective for VOCs</li> <li>• ineffective above 260°C</li> </ul>
sodium-aluminium silicates.	<ul style="list-style-type: none"> <li>• good for the removal of carbon dioxide, hydrogen sulphide, sulphur dioxide</li> </ul>	<ul style="list-style-type: none"> <li>• generally not effective for VOCs</li> </ul>

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Granular activated carbon is by far the most extensively used adsorbent in the chemical industry. It has proved to be effective in a wide variety of situations and compared to other adsorbents it is relatively cheap.

### Chemical characteristics of the gas stream

As it is the most widely used adsorbent in the chemical industry this section has been written from the perspective of GAC's ability to deal with types of substance. Activated carbon and macroporous polymers will have broadly similar strengths and weaknesses whilst zeolites, silica gel and silicates will be more appropriately used for polar compounds.

Certain types of substance are particularly amenable to adsorption by GAC. These include:

- those with relatively high molecular mass and/or boiling point (mass 45-140). Compounds with a mass below 45 are not readily adsorbed, those above 140 are not readily desorbed (HMSO 1994b). The USEPA (1996a/b) reports a slightly different range of 45-130;
- low polarity;
- cyclic rather than linear molecules;
- unsaturated rather than saturated compounds;
- compounds with a low volatility.

Above concentrations of about 10000 ppm the efficiency of adsorption drops off rapidly. In general below this concentration, the release level achieved is not dependent upon the concentration of the VOC in the gas stream.

However, not all substances that are readily adsorbed are as easy to desorb and thus recover. This may be because the:

- energy requirements required to separate the pollutant from the adsorbent are excessive. The higher the boiling point and/or the mass of the pollutant, the more energy is required to remove it. Examples include, nitriles and phenols;
- adsorbent may catalyse the decomposition of the pollutant, preventing its recovery as well as reducing the operational life of the adsorbent. For example, cyclohexanone tends to polymerise on GAC;
- certain compounds, in particular ketones, may present a combustion risk because of the large amounts of heat that they liberate during the adsorption process. Where such compounds are present it may be more appropriate to use a polymer based adsorbate. Whilst these are up to ten times more expensive than GAC they do not have the flammability problems when adsorbing ketones and thus the need for complex and expensive nitrogen blanketing systems for the desorption process is removed;
- the wider the variety of VOCs that are present in the gas stream, the more likely that non-uniform adsorption will take place, with one compound being preferentially adsorbed. This may lead to a chromatographic effect within the bed and may ultimately allow the other compounds through unabated.

### Physical characteristics of gas stream

Good adsorption is promoted by:

- low flow rates and low temperatures. These increase the effectiveness of the adsorption process, although if they are too low, adsorption may become insufficiently fast to match the emission from the process. Optimum operating temperatures are in the range 15-40 °C;

- increased pressure can improve adsorption efficiencies;
- minimising moisture and particles in the gas stream, both of which may blind, and thus reduce the availability of, adsorption points. At low VOC concentrations (typically below 1000 ppm) relative humidities above 50% may adversely affect the effectiveness of adsorption. At higher concentrations the influence of humidity is reduced;
- uniform airflow distribution to ensure that the full capacity of the adsorbent is utilised;
- sufficient capacity of adsorbent to deal with projected air flows and pollutant concentrations;

Pre-treatment of the gas stream may be necessary to ensure that these requirements are achieved, although this usually adds to the overall cost and complexity of the system. For example, fabric filters can be used to remove particulates and condensation can be used to reduce high VOC concentrations and cool the temperature of the gas. Note, the use of wet scrubbers to remove particulates may increase the humidity of the gas stream and thus reduce the effectiveness of the adsorption technique.

## Regeneration

The regeneration of the adsorbent is an important element of the operation of adsorption systems. The regeneration technique applied will in the first instance depend upon the type of adsorption system that is being used i.e whether or not it is a fixed bed process or based on continuous adsorption-desorption (capture systems will not generally be regenerated on site and as such are not covered by this study).

Each of these approaches is discussed below. It should be noted that regeneration never removes totally the adsorbed VOC. A residue (the heel) is always left behind and over time this will reduce the operational efficiency of the bed. The USEPA (1995) reports that 3-5% of organic material adsorbed to virgin activated carbon is likely to be left behind by desorption. The potential for reduced efficiency should be borne in mind and over time it may necessitate a reduction in the time that the bed is in use before regeneration. Eventually a new bed will have to be fitted and the old bed sent for specialist regeneration. The time intervals involved will be entirely dependent on the VOCs and flows involved and it is for the process operator and his suppliers to develop a suitable response to any reduction in removal efficiency.

## Fixed bed

A number of options exist for regenerating saturated fixed beds. These include:

- **Thermal swing.** The temperature of the bed is elevated to desorb the VOCs. The most frequently used approach is to pass saturated steam (at 100-110 °C) through the bed, removing the pollutant. A condenser is used to return the pollutant/steam mixture to the liquid phase. Separation of the pollutant from the steam will depend upon their miscibility. For those that are immiscible decanting may be an option, otherwise some form of distillation may be required. After steam cleaning the bed



needs to be allowed to cool and dry before it can be used again. This is usually achieved by the use of a stream of cool, dry air. Mycock (1995) lists a number of particular advantages of steam stripping, these include:

- at high pressures steam can desorb most VOCs without damaging them or the adsorbent;
  - steam readily condenses on the bed thus improving the efficiency of the release of its heat of condensation which in turn drives the desorption process;
  - condensation and/or distillation can be applied to separate a wide variety of VOCs from water;
  - residual moisture is easily removed by cool, dry air;
  - steam is a more concentrated source of heat than hot air and thus more effective at raising the temperature of the bed.
- **Inert gas.** Hot inert gas (usually nitrogen at 200-300 °C) is passed through the saturated bed. The gas initially removes any moisture on the bed and this in turn can be removed by passing the inert gas through a molecular sieve. Once any moisture is removed, the inert gas strips out the pollutant, which is then recovered by condensation. This system has the advantage of recovering relatively pure pollutant, with a low moisture content as well as potentially reducing energy demands compared to steam regeneration;
  - **Vacuum.** A vacuum is applied to the bed which allows the pollutant to be re-vaporised. The pollutant is then removed from the system by back-purging and subsequently recovered by condensation. Although vacuum systems are particularly useful for the recovery of less volatile compounds, they also tend to be more expensive than other regeneration options;
  - **Displacement cycle.** This is an infrequently used approach whereby the adsorbed material is preferentially displaced by another material. It will only be applied when the adsorbate is both temperature sensitive and valuable and vacuum desorption is ineffective (Mycock 1995);

Steam regeneration is the most widely used technique in the chemical industry, being both cheap and easy to apply. Steam is also widely utilised in this sector and is thus likely to be available for desorption purposes. Inert gas systems are generally more expensive but will typically provide better quality VOCs which, unlike steam regeneration, may not require a further purification stage prior to being re-used. Vacuum desorption systems are more expensive and complex again and will tend only to be used under specialist conditions.

### **Continuous adsorption-desorption**

In rotating systems the desorption stage may be based on either steam or hot, inert gas and the comments made above about these desorption approaches are generally applicable.

In tower systems the desorption system is usually based on hot, inert gas.

## Control of adsorption techniques

Traditionally adsorption beds were operated for fixed periods of time before being regenerated. Thus occasionally beds may have been operated when already saturated with the result that pollutant passed through the bed unabated. In the converse situation less than fully saturated beds were removed from use and regenerated with consequent waste of energy.

More recently, however, instrumentation has been developed that allows beds to be switched when the concentration of the pollutant in the exit gas reaches a pre-determined level. Bed performance can also be monitored by measuring the pressure drop across the bed. The pressure across a bed should remain roughly constant, variations indicate that performance is deteriorating, for example because the bed is breaking down.

Although fixed beds are designed to be re-generated a number of times, they will eventually need to be replaced or removed for specialist off site cleaning. The frequency of this operation will depend upon the throughput of the system and the types of chemical it is handling.

There is a risk of fire whenever carbon adsorption beds are used, particularly when the gas stream contains oxygen and compounds that are easily oxidised by carbon, for example ketones, aldehydes and organic acids. Whenever such compounds are present particular care will be needed when operating and re-generating the bed.

Careful control may also be required when adsorption techniques are being used with batch processes. There is a risk that VOCs adsorbed onto the bed whilst the process is operating may be desorbed when the bed is out of use. To prevent this happening it is important to ensure that gas flow is diverted away from the bed during intervals when no production is occurring.

## Conclusions

Compared to other techniques there are a large number of gas stream characteristics (moisture, particulates, temperature, presence of mixtures of VOCs etc) that may reduce the effectiveness of adsorption, characteristics that are particularly prevalent in batch operations. A number of these characteristics can be modified by pre-treatment of the gas stream but this will tend to increase the technical complexity and economic cost of the technique.

A fixed bed system utilising a granular activated carbon adsorbent and steam based regeneration is by far the most widely used combination currently used in the sector. In general operators will only tend to deviate from this combination when the characteristics of the particular gas streams that they generate are not amenable to treatment in this manner. For example, for gas streams with a high, relatively constant VOC loading, the enhanced mass transfer characteristics of fluidised fixed beds or continuous adsorption/desorption beds may be more appropriate

Activated carbon mats and polymer based systems offer some advantages as adsorbents when compared to granular activated carbon. However, their relatively high costs does to a large extent limit their applicability. Inert gas regeneration may offer some advantages compared to the use of steam, in particular the better quality of the recovered VOC, but again this needs to be balanced with the increased cost associated with its use.

In general, adsorption systems will be wider and flatter than other techniques, with perhaps the exception of certain biological oxidation systems. If size is a constraint for the process then this may have to be taken into account.

### 6.1.5 Condensation

Condensation involves the removal of one or more volatile components from a gas stream by saturation followed by phase change. Condensation is facilitated by decreasing temperature or increasing pressure. Most condensation systems use the former, changing the pressure of large volumes of gas can be extremely expensive.

Unlike adsorption and absorption no chemical or physical interaction is required between the pollutant and the abatement system. Consequently condensation techniques can in theory be applied to any pollutant in any gas stream. In practice the main constraint on their use is the temperature that has to be achieved to allow condensation to occur. If the temperature required is particularly low, the energy required to achieve this temperature may mitigate against its use. Particularly low temperatures will be required for gas streams containing:

- low boiling point pollutants;
- low concentrations of pollutants;
- high concentrations of non-condensable material.

Lower temperatures will also promote improved removal efficiencies.

Condensation techniques have been widely utilised in the chemical industry. In particular they have been extensively applied to reactor vents where the condensed liquid can be returned directly to the reaction or as a pre-treatment step for other abatement techniques whereby they reduce high concentrations to more manageable ones. Both of these uses have tended to require temperatures between 0 °C and ambient but as the technology has improved and the attainment of lower temperatures been achieved so it has proved possible to apply condensation techniques as primary abatement.

As the ability to achieve low temperatures in a cost effective manner is the main limitation on their use this has also been the main restriction on their availability. A number of different condensation techniques are available. The main ones are:

- coolant/refrigeration;
- cryogenic nitrogen.

The main difference between the systems is the operating temperature that they can achieve.

The merits of these systems are discussed below but before doing so a brief discussion is provided of some of the more generic issues that apply to both systems. These include:

- the prevention of fog formation;
- minimising energy requirements;
- reduction in efficiency due to freezing on condenser walls.

Fog formation arises when droplets that condense out of the gas stream have insufficient time to reach the cold surface of the condenser. Instead they are suspended in the exhaust gas and may give rise to a mist or fog at the release point to the environment. Fog formation can be minimised by ensuring that the heat transfer surfaces are adequately sized, using a series of condensers to minimise the heat differential between the gas stream and the heat transfer agent, using a demister or reducing the gas velocity in the condenser.

Because cooling the gas stream can be an energy intensive process it is often more efficient to pre-cool the incoming gas stream using the chilled exhaust stream from the main condenser. This is then followed by an intermediate chilling stage and then the main condenser.

Pre-cooling can also remove higher boiling point components (such as water and hydrocarbons) which when they freeze can 'ice' over the primary condenser reducing the efficiency of removal of the target pollutant. As an alternative to pre-cooling, the system can be periodically cleaned by circulating air through it or two or more condensers used in parallel with one operational and one 'thawing' at any one time.

Water may also occasionally cause a problem associated with the formation of azeotropes with the target VOC. In such cases the temperature at which the azeotrope condenses may be lower than that of either of the individual components and the condenser needs to be designed accordingly, or the water removed prior to condensation.

### **Coolant/refrigeration**

These systems have been widely applied in the chemical industry, with a diverse range of coolants/refrigerants being available to cover the temperature range of ambient to about 70 °C, yet they cannot achieve the low temperatures demonstrated by cryogenic nitrogen systems.

Either indirect cooling or direct cooling of the gas stream can be used. Direct cooling generates an additional need to separate the coolant from the VOC and so is rarely used these days. It is only really viable when the contact coolant is the same compound as the one which requires removal from the gas stream.

Indirect cooling is typically based on the passage of the gas stream over tubes containing the coolant. The VOC condenses on the exterior wall of the tube and drains to a collection tank beneath the tubes. The VOC can then be reused or sent for a further purification stage, for example distillation.

The coolant used depends upon the temperature that is required to remove a particular target pollutant(s). Thus for low volatility substances that condense with relative ease air or water systems may be appropriate. For lower temperatures chilled water, air or brine may be used, whilst glycol or liquid methanol may offer further reductions in temperature.

Variations on the traditional shell and tube system include spiral heat exchangers, which whilst more difficult to maintain have operational advantages, such as smaller space requirements, and condensation filtration. The latter is particularly effective for high boiling point VOCs but has yet to be widely demonstrated in the chemical industry.

The lower the desired temperature, the greater the associated costs of installing and, in particular, operating the technique are likely to be. Thus as the desired temperature reduces the more important becomes the management of the energy requirements of the system. This can mean that when particularly low temperatures are required, the system is only likely to be economic with fairly constant flow rates that minimise the cycling of the refrigeration system's compressors and thus consequent energy requirements and costs. Multi-stage refrigeration units can be used as a means of efficiently reaching low temperatures. The Environmental Technology Best Practice Programme (ETBPP) has recently brought out a guide on improving the energy efficiency of heat exchange operations (ETBPP 1997c).

### **Cryogenic nitrogen**

Cryogenic nitrogen systems have only recently been demonstrated on an industrial basis. Cooling is achieved by the evaporation of liquid nitrogen to form nitrogen gas. They can achieve significantly lower temperatures than coolant/refrigerant systems and thus can be applied to a wider range of compounds and achieve better removal rates. However, this has to be balanced with their generally greater capital and operating costs.

Cryogenic nitrogen condensation systems are based on nitrogen induced cooling and thus their use may be particularly effective at sites that have already installed nitrogen systems, for example to provide inert storage/reaction conditions. Prior to installation an assessment of the site's nitrogen balance needs to be undertaken to identify whether nitrogen use is similar to the cooling requirements of the condensation system. The necessary balance is usually easier to achieve for continuous operations where long term nitrogen requirements and the flow/concentration/VOCs requiring treatment can be predicted relatively well. For batch operations it may be harder to quantify the balance and it may be necessary to average out the various flows over a set time period.

Provided liquid nitrogen is used on site and the correct balance can be achieved there appear to be a number of advantages in applying cryogenic nitrogen systems. These include:

- all VOCs can theoretically be removed from a gas stream to better than 99%. However, the lower the temperature required to remove a specific VOC and the better the desired release level the greater the burden placed on the nitrogen system;
- there is considerable future proofing built into the system. Thus if future regulation demands it, release levels can be tightened by reducing the condensation temperature whilst any VOC that may be introduced in the future can be dealt with. Again the site's nitrogen balance will dictate whether or not these theoretical improvements can actually be achieved;
- moisture and particulates are generally not issues for the system. Moisture can be removed from the gas stream with relative ease by the use of a coolant based pre-condenser or heat exchangers operating in parallel and particulates will only need to be removed if they are 'sticky' and thus may foul the heat exchange surface;
- systems can be designed to deal with the fluctuations in flow and concentration that characterise this batch-based sector. Provided the nitrogen balance is correct the rate

of evaporation of liquid nitrogen can be rapidly varied to deal with changing process conditions;

- the condensed VOCs are not contaminated with other materials as is the case with, for example, steam regenerated adsorption and certain scrubber systems which will recover the VOCs into water. However, if, as is often the case in this sector, the VOCs are present as a mixture, separation into the mixture's constituent parts will still be required if reuse/recycle is to be facilitated. If separation is not technically and/or economically feasible then the recovered mixture will have to be disposed of.

Additional benefits may arise from the use of nitrogen as the carrier gas for the waste VOCs. The use of nitrogen in this manner allows a more concentrated gas stream to be treated by reducing problems associated with the lower explosive limit (LEL). A more concentrated flow reduces capital and operating costs.

The ETBPP (1996b) notes that for flows greater than 5000 m<sup>3</sup>/hr cryogenic nitrogen systems are generally not feasible because of the costs associated with evaporating the necessary nitrogen.

The presence of acid gases in the gas stream to be treated may necessitate the construction of the condenser out of corrosion resistant materials or the installation of pre-scrubbers. The latter approach is usually favoured on cost grounds.

A recent innovation to reduce the cost of operating a cryogenic systems is based on the use of constantly cycling steel balls. The steel balls are indirectly cooled by nitrogen before passing through the gas stream. The target pollutants condenses on the cold surface of the steel balls. The steel balls pass through a cleaning phase where the condensed pollutant is removed and then pass back into the cooling phase of the system.

The use of constantly moving steel balls significantly reduces the problems caused by stationary heat exchange surfaces icing up, which necessitates regular shut down of the plant or the installation of two or more heat exchangers. This technique is reported to work well in the concentration range 10 - 1000 g/m<sup>3</sup> (IEM 1997).

### **Closed-cycle inert gas**

Closed-cycle inert gas systems have primarily been used in association with drying ovens in coating processes. These processes typically give rise to higher concentrations of pollutant than are found in the sector of interest. At these high concentrations the inert gas allows the explosive limit of the gas stream to be increased, thus enabling more concentrated streams to be treated and consequently more pollutant to be removed per unit of flow of gas stream. The circulating inert gas stream is passed through a condenser, the type selected will depend upon the VOC involved and thus the required temperature, where the VOC is recovered and the nitrogen passed back into the drying oven.

## Control of condensation techniques

Condensers are generally easier to control than other techniques, with the outlet gas temperature being the main indicator of removal efficiency.

## Conclusions

Condensation is a relatively simple technique for recycling VOCs. In general condensers are cheap to install and easy to operate, although the operating costs may be high if low temperatures need to be achieved. They are particularly amenable for use with high concentrations of VOCs, although they will often require a secondary, downstream control technique to be applied to achieve low release levels.

Recent innovations in cryogenic nitrogen systems mean that lower temperatures can now be achieved on a consistent basis. This means that a broader range of pollutants can be dealt with using this technique and that better removal rates can be achieved. However, the low temperatures required by these systems can only be generated by nitrogen systems, which are expensive to construct and operate. Thus unless a nitrogen plant is already operated at a site or its installation would serve more than one purpose it is unlikely that the costs associated with its installation for cryogenic condensation purposes alone could be justified in all but a few cases. If a nitrogen plant is already in operation it may be appropriate to undertake a preliminary estimate of the site's nitrogen balance to assess whether the installation of a cryogenic condensation system is feasible.

### 6.1.6 Absorption

Absorption is based on the mass transfer of the pollutant between the gas stream and a scrubbing liquor or the direct chemical reaction between the same. Mass transfer, but not chemical reaction, systems offer recycling possibilities, although the product of the chemical reaction may itself occasionally be utilised for a different purpose.

Perhaps the most important criteria in deciding whether to use absorption is the availability of a suitable scrubbing liquor which will preferentially remove the pollutant from the gas stream or react with it. For chemical reaction a suitable reagent is required to react with the pollutant, for this reason these systems are often used to treat acids or alkalis, for which a wide range of neutralising compounds are available.

Absorption techniques have been widely used in the sector. They may be particularly effective for the control of discontinuous emissions from batch processes as it is relatively cheap and easy to bring them back up to full operating efficiency.

The main variables in selecting an absorption systems are the:

- physical characteristics of the gas stream;
- chemical characteristics of the pollutant and the scrubber liquid;
- process unit design for contacting VOC with scrubber liquid.

This range of variables means that absorption systems can be relatively complex to design. Each are discussed below.

Although absorption can be used as a technique for dealing with both particulates and VOCs, Mycock (1995) reports that systems cannot usually be optimised to deal with both problems at the same time. In the former case removal efficiencies are promoted by short residence times, in the latter case the reverse is true.

### **Physical characteristics of gas stream**

The lower the temperature of the gas stream, the lower the partial pressure of the pollutant and thus the greater the pressure differential with the scrubber liquid and the better the transfer. In addition, high temperatures increase the risk of losses due to evaporation (USEPA 1995).

### **Chemical characteristics of pollutant and scrubber liquid**

If no effective absorption liquid can be identified for a pollutant, then this will not be an effective recovery/treatment option. In addition, at low concentrations of VOCs (typically below 200-300 ppm) the rate of mass transfer between the gas and liquid phases becomes too slow for this approach to be efficient.

Many absorption systems use water as the scrubbing liquid, in which case the target pollutant needs to have at least partial water solubility. As the solubility of the target pollutant in water reduces so the amount of water and contact time required increases, resulting in the need for excessively large, uneconomic systems. Polar organic compounds (for example those containing nitrogen, sulphur and oxygen) are therefore particularly amenable to removal using water based absorption systems. Increasing molecular weight of the target compound will reduce its solubility in water.

Absorption systems are available for dealing with non-water soluble compounds. These systems make use of a non-volatile organic scrubber liquid (volatile liquids may be entrained in the gas stream and exhausted to the environment) such as mineral oil. However, these systems are relatively expensive because separation of the mineral oil from the target pollutant is energy intensive. Once-through non-water based systems are not viable because of the economic cost of the mineral oil and the difficulties of treating the resulting effluent. In a few situations it may be feasible to use the VOC contaminated oil as a fuel. The USEPA (1995) notes that oil based absorption systems only tend to be utilised when there is a plentiful supply of oil on a site e.g in refineries and petrochemical plants.

If the scrubber liquid and the target pollutant react, absorption can still be used to remove the pollutant from the gas stream but recovery will not be option. Absorption based on reaction is usually applied for the neutralisation of acid or alkali gas streams.

Absorption systems can also be used to facilitate odour control, where the absorption liquid is a chemical such as potassium permanganate or sodium hypochlorite. Recent innovations have seen the introduction of a catalysed absorption process that leads to the oxidation of the odorous compound. This system allows better odour removal efficiency as well as broadening the range of compounds that can be dealt with in this manner.



In selecting scrubber liquids, operators need to be aware of the following issues:

- if a non-water based scrubbing liquid is to be used there is the potential for it to be volatilised and lost to the environment. In general, therefore, organic scrubber liquids will need a boiling point of at least 190 °C when the technique is operating at ambient temperature;
- the scrubber liquid needs to have an effective life in the system and therefore should not be susceptible to thermal or chemical degradation;
- columns operate most efficiently at low temperatures but if the temperature is too low many liquids become viscous and do not spread well, reducing the efficiency of the system;
- flammable, toxic and odorous compounds should generally be avoided;
- if the target VOC is poorly soluble then the volume of scrubber liquor required to allow mass transfer may be so great that the size of the system becomes economic.

### **Process unit design for contacting VOC with scrubber liquid**

The design of the process unit selected for use will depend upon the chemical and physical characteristics of the gas stream to be treated as well as the desired removal efficiency. All systems try and maximise the interfacial contact between gas and liquid phases and leave sufficient contact/residence time to allow phase transfer/reaction. Thus many absorption systems are based on breaking up the scrubber liquid into droplets or a film.

A wide range of process units are available, these include:

- Packed towers. These use packing (porcelain, metal, plastic etc) to provide a large surface area on which mass transfer can take place. The packing may be added to the tower randomly or uniformly. In the latter case care needs to be taken to ensure that distributors are installed on the tower's walls to ensure uniform wetting of the packing. Packed towers can be constructed out of chemically resistant materials to deal with corrosive gas streams. The USEPA (1995) reports that packed towers are the most widely used for pollution control they can achieve better removal rates than other towers and generally utilise less water. They can also be designed to have a relatively long contact time which means that they may be particularly appropriate for pollutants that are poorly soluble in the absorbate. However, the USEPA (1995) also reports that the presence of particulates in the gas stream can cause blockages between the packing material reducing the flow through the column and thus reducing removal efficiencies. In addition, they tend to have higher pressure drops and maintenance requirements than other systems. Packing may be metal (cannot be used in corrosive environments), plastic (cannot be used in high temperature environments) or ceramics (rarely used these days because of their brittleness);
- Moving or fluidised bed. This works on the same principle as the packed tower, with in this case the fluidised bed, usually hollow plastic spheres supported by the incoming

gas stream, providing the large surface area for mass transfer. Fluidised beds have the advantage over packed towers of being less susceptible to the presence of particulates but are more expensive to construct and operate;

- Plate towers. These use a series of plates to disperse the gas stream into numerous bubbles which maximises the area for mass transfer. They are particularly effective for large scale operations where a low liquid flow rate is desired. They are also good for dilute wastestreams or wastestreams with relatively high concentrations of particulates. However, they can have very high pressure drops and when corrosive materials are present the cost of protecting them may be higher than for packed towers (USEPA 1995);
- Impingement plates. These also contain plates but use a series of additional impingement plates above the perforations in the main plates of the column. When the gas stream hits these impingement plates it is deflected imparting additional turbulence and promoting enhanced mass transfer;
- Spray towers facilitate mass transfer by atomising the absorbent. They are relatively easy to install and operate and can be constructed out of chemical resistant material to deal with corrosive gas streams. The presence of particulates in the gas stream can lead to the atomising nozzles becoming blocked. Of all the delivery systems they have the least effective mass transfer capability and their use is generally restricted to removal of particulates and high solubility gases such as sulphur dioxide and ammonia;
- Venturi scrubbers provide good gas/liquid mixing and are good for particulate removal but they require large pressure drops, and so are energy intensive. This coupled with their short contact time means that they are not particularly effective for VOC removal;
- Wet mop scrubbers and rotacloves operate on the same principle as each other with the absorbent being injected into a spinning brush arrangement to atomise it. Wet mops tend to have a flexible atomising arrangement, rotacloves a rigid one;
- Void towers use gravity to drop the scrubber liquid through a large number of meshes. They are generally small and cheap to install and operate but they are best applied when the VOC is very soluble in the scrubber liquid.

### Control of absorption systems

One of the main strengths of absorption systems is the number of variables that can be manipulated to ensure optimum performance. These variables include:

- temperature of gas and scrubber liquid;
- circulation rate of the scrubber liquid;
- design of column.

A flow indicator with alarm should be installed to check that the scrubber liquid is still flowing. A monitoring device should also be fitted to check the composition on the exhaust gas.

The potential formation of a visible plume in the exhaust gas may also require control. This results from the gas stream temperature being cooled to its saturation temperature. Potential controls include the fitting of a demister or a knock out pot. Mycock (1995) suggests that as a general rule of thumb the exhaust gas temperature should be at least 15 °C above its dew point.

## Conclusions

Absorption as a technique has been widely applied in the sector. It is an extremely flexible technique being able to deal with a wide range of operating conditions, such as variable flow and concentration. Compared to other techniques it is not particularly sensitive to the presence of a wide range of compounds in the gas stream and the presence of moisture and non-condensables.

It has been applied to the control of VOCs but the need to identify a suitable solvent in which the VOC is soluble may be a problem. In addition, if BPEO problems are not to be caused, a suitable mechanism for recovering the VOC from the solvent needs to be found.

### 6.1.7 Thermal processes

Thermal processes rely on the thermally induced breakdown (oxidation) of pollutants. Complete oxidation results in the formation of carbon dioxide and water. Incomplete oxidation can result in the formation of other organic compounds such as aldehydes or acids (USEPA 1995).

The main thermal processes are:

- (high temperature) thermal oxidation;
- (low temperature) catalytic oxidation;
- flameless thermal oxidation;
- flares.

The latter is not typically used in the sector but is briefly discussed here.

### Thermal oxidation

Pollution control aspects of the use of incinerators for the destruction of chemical wastes are discussed in the Process Guidance Note on Waste Incineration (S2 5.01) (HMSO 1996b). The main issues of relevance to this sector are:

- compared to other techniques it can achieve very good removal efficiencies under a wide variety of conditions;

- a supplementary energy source may be required to support the oxidation of VOCs with a low heat content or dilute flows;
- the heat generated from incineration can often be put to useful benefit. For example, to pre-heat the incoming gas stream or in process driers;
- oxidation will probably be appropriate where recycling is not feasible. For example, where the gas stream contains a wide variety of VOCs or is contaminated in some other way;
- highly variable flows may reduce the efficiency of oxidation. The use of concentrators (for example adsorption systems) may allow the flow to be evened out over time;
- safety devices will be required, for example flame arrestors, to provide a screen between the process and the abatement technique;
- oxidation may give rise to secondary pollutants such as acid gases that require subsequent treatment;
- the USEPA (1995) reports that above 2000 ppmv it is more appropriate to describe removal efficiencies in terms of a 98% percentage reduction in the VOC content of the gas stream rather than the limit value of 20 ppmv that should be achievable for all new oxidisers for inlet streams containing less than 2000 ppmv.;
- the key measure of removal efficiency is the temperature of the combustion chamber.

### **Catalytic oxidation**

Catalytic oxidation uses a catalyst bed to promote the oxidation process at a lower temperature than is required by thermal oxidation. This has the advantage of reducing:

- auxiliary fuel requirements. Mycock (1995) reports that catalytic oxidation can reduce auxiliary fuel requirements by 40-60% compared to thermal oxidation;
- the need for the oxidiser to be constructed out of expensive and heavy high temperature proof materials;
- the chance of secondary pollutants such as NO<sub>x</sub> being formed.

However, they have certain disadvantages compared to the use of thermal oxidation, in particular catalytic oxidisers are susceptible to poisoning and/or blinding by constituents of the gas stream. Metals in particular (arsenic, antimony, lead, mercury etc) are catalyst poisons, whilst particles may not only blind but also abrade the surface of the catalyst. The surface of the catalyst can be periodically washed but this will give rise to a contaminated waste water stream. Excessive temperatures may also damage the catalyst. Mycock (1995) notes that all catalysts, however well protected, eventually degrade with a resulting decrease in removal efficiency. A well managed catalyst could typically be expected to last 3-5 years, although there may be considerable variation in specific cases.

In addition, fluctuations in VOC concentrations may damage the catalyst bed. A concentrator (e.g adsorption bed) prior to the oxidation chamber may allow fluctuations to be averaged out. The USEPA (1995) also reports that the VOC content of the gas stream should be kept relatively constant and low enough to prevent excessive heating of the catalyst. A concentration range of 50-10 000 ppmv is quoted. Again a pre-concentrator can be used to even out fluctuations, although this will add to the overall cost and complexity of the technique.

Considerable work has been done by the manufacturers of catalytic oxidisers to develop catalysts to deal with a wide range of contaminants. This has reduced the number of potential poisons that totally rule out the use of catalytic oxidation. In particular, many of the problems associated with the presence of sulphur and chlorine have now been addressed. For example chrome/alumina, cobalt oxide, copper oxide/manganese oxides have all served as the basis for the control of chlorinated compounds by catalytic oxidation. Platinum based catalysts have also been developed to deal with sulphur containing compounds, although these catalysts are still susceptible to poisoning by chlorinated compounds. Compounds containing lead, arsenic and phosphorous are still fast acting poisons under virtually all conditions (USEPA 1995). Zinc and tin are also poisons but act slower than those mentioned above and thus there is more scope for dealing with them (Mycock 1995).

In addition, fluidised bed systems have been developed that allow a catalyst to be constantly replaced thus reducing the impact of poisons. From a BPEO perspective spent catalyst is removed as a waste that requires disposal. In addition, the USEPA (1995) reports that attrition of the catalyst in the fluidised bed may result in particulates being entrained in the exhaust stream with a consequent requirement for costly abatement particulate abatement equipment, such as a venturi scrubber, being fitted.

Despite these innovations poisoning is still an important issue. There are still a number of pollutants for which this technique is not appropriate. In addition, and perhaps most importantly, many process operators still view the technique as not being robust enough to justify costly investment. This may be particularly the case amongst the operators of batch processes where it is often difficult to plan with any great certainty what chemicals may be being utilised in future years. If one of these has the potential to act as a poison and the operator has gone to great expense to install a catalytic system then production of the compound may not be viable.

It may be possible to retro-fit catalytic beds to existing high temperature oxidisers. This may reduce operational costs and prolong the life of an existing thermal oxidiser.

Because the cost of a catalytic bed is directly proportional to the air flow to be treated then above a certain threshold, one manufacturer uses 20 000 m<sup>3</sup>/hr as rule of thumb, the economic advantages of using catalytic rather than thermal oxidation diminishes. In comparison, the larger the air flow treated by a thermal oxidiser, the greater the economies of scale that can be achieved.

## Recovery of energy

An important consideration in utilising a thermal technique is the potential it provides for the recovery of useful heat energy. This heat energy can be used to reduce the auxiliary fuel requirements of the thermal technique or be used in the process.

The heat released by the oxidation of VOCs in a thermal oxidiser directly reduces the need for auxiliary fuel irrespective of whether or not an engineered energy recovery system is installed. Energy recovery will, however, further reduce fuel requirements. Auxiliary fuel requirements in a catalytic oxidiser can only be reduced by the use of energy recovery. The lower the concentration of VOC in the gas stream, and thus the greater the potential need for auxiliary fuel, the more important becomes energy recovery.

Without the recovery of heat energy the operator may well find the economics of the thermal technique unacceptable. However, if an operator proposes to use a thermal technique without energy recovery then full environmental justification for this approach would be expected.

The main ways of recovering useful heat energy are:

- recuperative systems, which use a shell and tube or other type of heat exchanger to recover heat from the hot exhaust gas and use it to pre-heat the incoming gas stream or for some other process related purpose (e.g steam raising); or
- regenerative systems, which utilises two or more ceramic beds. The hot exhaust gas is passed over one bed, reducing the exhaust gas temperature whilst increasing that of the bed. Meanwhile the inlet gas stream is passed over the other ceramic bed, increasing the gas stream temperature whilst reducing that of the bed. The mode of the two beds is periodically swapped. When the beds are being swapped there is the potential for a small volume of gas to be released untreated. Purge systems have been introduced to deal with this problem. These consist of three or more beds such that at any one time the last bed to be used for heating the incoming gas stream is slowly being purged prior to being swapped over to exhaust mode.

The decision as to which energy recovery system should be utilised will be an entirely site selective one. For processes giving rise to low flows and relatively low concentrations heat recovery may not be cost effective.

## Control of thermal and catalytic oxidation techniques

The main issues to be considered in operating an incinerator are:

- the residence time of the gas stream in the combustion chamber. This will depend upon the required destruction efficiency of the chamber and may typically be of the order of 0.5-1 second;
- the operating temperature in the combustion chamber. This is typically about 200-400 °C above the auto-ignition temperature of the most stable VOC in the gas stream which usually results in combustion temperatures of 750-800 °C, although chlorinated compounds will require substantially higher temperatures. In the case of

catalytic combustion, the bed temperature will also be an important consideration. It would be expected that continuous monitoring of temperature will be used;

- turbulence in the combustion chamber. This ensures thorough mixing of the gas stream and promotes good combustion;
- the presence of moisture tends to increase the secondary fuel requirements;
- certain pollutants may need to be removed from the gas stream prior to incineration, in particular those that may foul/corrode the system or poison catalytic beds;
- an excess of air is required to provide sufficient oxygen to allow complete oxidation. Management of this air flow is very important. Too much air leads to the size, and cost, of the oxidiser increasing, whilst auxiliary fuel requirements are also increased. Too little and the oxidation process is incomplete leading to the release of pollutants to atmosphere;
- suppliers can usually provide a fairly good estimate of removal efficiencies prior to installation but these should be verified on completion of the construction phase and before routine operation commences.

Most problems associated with thermal oxidisers have traditionally arisen from poor burner operation and poor start up/shut down procedures. It is therefore important that the operator can demonstrate that robust operating procedures, including good monitoring and maintenance programmes, are being utilised.

### **Flameless thermal oxidation**

Flameless thermal oxidation makes use of an inert, hot ceramic matrix to support the oxidation process. Once combustion of the gas stream has been initiated radiation and convection transfer heat to the incoming gas stream, raising its temperature to the ignition point.

Unlike other types of oxidiser no flame is present and so the potential for the formation of NO<sub>x</sub> and dioxins is reduced (USEPA 1995). They also have lower secondary fuel requirements than conventional oxidisers. In addition, the large thermal mass of the ceramic packing allows the technique to store or release large amounts of heat without rapid changes in temperature. They may therefore be particularly suited to dealing with fluctuating flows and concentrations characteristic of this sector. Removal efficiencies of 99.99% are claimed (EBM 1997). A very wide range of air flows can be handled ranging from 5-100 000 m<sup>3</sup>/hr.

Particulates will usually have to be removed from the gas stream prior to it entering the oxidiser and in the presence of chlorinated or sulphur based compounds there will still be the potential for acid gases to be formed with consequent exhaust gas scrubbing requirements.

### **Flares**

HMIP produced a Technical Guidance Note on flaring in 1993 (HMSO 1993g). This Note should be referred to for a general discussion of the topic. Flaring is not widely practised in the

fine and speciality chemicals sector and any operator in this sector that utilises it would be expected to provide robust justification.

Prior to installation, the characteristics of the gas flows that the flare will have to deal with should be considered, of particular relevance will be the substances present and their heat content. If insufficient heat content is present, a secondary fuel source will be required. The injection of steam or pressurised air may also be required to promote the necessary turbulence to allow complete combustion.

Flaring does not allow as good a control as other forms of thermal destruction and may cause corrosive or harmful by-products to be formed. This is a particular concern when organochlorine and sulphur containing compounds may be present in the gas stream and the use of flaring to control such compounds would not normally be considered to be acceptable.

Flares may be used as control measures for emergency releases where there is too much gas involved to allow the use of dump tanks etc but the flow is insufficient or too intermittent to justify the fitting of an abatement technique.

## **Conclusions**

Thermal oxidisers have been used to treat VOC emissions from the chemical industry and generally achieve very good release levels. They can be utilised under a wide variety of conditions and are not as susceptible to moisture or particulates in the gas stream as are most other techniques. Thermal oxidation may be particularly appropriate for gas streams containing a wide range of compounds. It can also deal with odour problems.

The primary drawbacks to the use of thermal oxidation are the inability to recycle and the costs of installation and operation. Some of the operational costs can be reduced by the use of heat recovery. SO<sub>x</sub> and NO<sub>x</sub> emissions may also be problematical under certain operating conditions.

Catalytic oxidation offers a number of advantages compared to thermal oxidation. In particular lower oxidation temperatures mean that operational fuel use and construction costs are lower. However, in general they do not give quite as good removal efficiencies and they cannot deal with as broad a range of flows, concentrations and fluctuations as thermal oxidisers. They are also susceptible to catalyst poisoning and blinding which may require pre-treatment of the gas stream but developments in catalysis has reduced the number of instances when their use is totally precluded.

### **6.1.8 Biological oxidation**

This is a destructive technique that relies on the biologically induced oxidation of VOCs to form water and carbon dioxide. The main biological systems for the control of VOCs are (Khan 1997):

- biofiltration, where the gas stream is passed through a moist substrate (peat, heather etc), which supports the micro-organisms;



- bioscrubbing, where the gas stream is passed through a trickling filter or column;
- bioreactors, where the micro-organisms are supported on an artificial substrate in a reactor.

All three systems operate on the same basic premise, that certain organic compounds can be readily biodegraded by micro-organisms.

The respective strengths and weaknesses of biofilters and biosystems have been summarised by the DTI's Biotechnology Means Business Initiative (BMB 1998) and are reproduced in Table 6.2 below, no information is provided on bioreactors.

**Table 6.2 Summary of strengths and weaknesses of biological systems**

System	Application	Strengths	Weaknesses
Biofilter	<0.5 g/m <sup>3</sup>	<ul style="list-style-type: none"> <li>• high gas/liquid surface area</li> <li>• works for VOCs and odours of medium solubility</li> <li>• easy operation and start up</li> <li>• low operation costs</li> </ul>	<ul style="list-style-type: none"> <li>• poor control of reaction conditions</li> <li>• slow adaptation to fluctuating concentrations in gas stream</li> <li>• large area required</li> </ul>
Biotrickling filters	<0.5 g/m <sup>3</sup>	<ul style="list-style-type: none"> <li>• comparable to bioscrubbing</li> <li>• better retention of slow growing micro-organisms</li> <li>• single reactor</li> </ul>	<ul style="list-style-type: none"> <li>• low surface area for mass transfer</li> <li>• higher operational costs than biofilters</li> <li>• potential clogging</li> </ul>
Bioscrubbers	<3.0 g/m <sup>3</sup>	<ul style="list-style-type: none"> <li>• better control of reaction conditions (pH, nutrients)</li> <li>• possibilities to avoid accumulation of products</li> <li>• compact equipment</li> <li>• low pressure drop</li> </ul>	<ul style="list-style-type: none"> <li>• low surface area for mass transfer</li> <li>• disposal of excess sludge</li> <li>• extra air supply needed at high degradation rates</li> <li>• higher investment and operational costs</li> </ul>

Biofilters tend to have a low efficiency and thus more usually applied to deal with odours and low concentrations of VOCs. Bioscrubbers provide better mass transfer than biofilters and are thus able to deal with higher concentrations of VOCs. Bioreactors are more efficient than both biofilters and bioscrubbers and also tend to be more compact, but they are more sensitive to fluctuating flow and concentrations (Khan 1997).

### VOCs that can be destroyed by biological oxidation

In theory any VOC can be biologically oxidised but in practice the time taken to oxidise certain compounds (the residence time) precludes their control by this method. Mycock (1995) has summarised the biodegradability of some VOCs and this is reproduced in Table 6.3.

**Table 6.3 Biodegradability of VOCs**

Relative speed of biodegradation	VOC
Rapid	<ul style="list-style-type: none"><li>• alcohols</li><li>• aldehydes</li><li>• amines</li><li>• organic acids</li></ul>
Good	<ul style="list-style-type: none"><li>• esters</li><li>• ketones</li><li>• phenols</li><li>• mercaptans</li></ul>
Slow	<ul style="list-style-type: none"><li>• aliphatic hydrocarbon</li></ul>
Very slow	<ul style="list-style-type: none"><li>• halogenated hydrocarbons</li><li>• polyaromatic hydrocarbons</li></ul>

Mycock (1995) summarising the work of Yavorsky made the following general points:

- aliphatic compounds containing an oxygen molecule and less than seven carbon atoms are very degradable. Examples of such compounds include ethanol, acetone, isopropyl alcohol, methyl formate and methyl ethyl ketone. Control efficiencies greater than 95% are possible in very short intervals (approx. 1 minute) for concentrations around 1500 mg/m<sup>3</sup>;
- aliphatic compounds with more than six carbon atoms and aromatic compounds such as toluene, xylene, phthalates etc are moderately degradable. Control efficiencies of 95% are possible for inlet concentrations up to 500 mg/m<sup>3</sup> with retention times of several minutes. Higher concentrations and/or control efficiencies can be achieved but only with longer retention times;
- chlorinated hydrocarbons containing one or two chlorine atoms (e.g methyl chloride, 1,2 dichloroethane) can be degraded at inlet concentrations less than 20 mg/m<sup>3</sup>.

The BMB (1998) notes that the water solubility of the VOC is very important. The process of biological oxidation is dependent on the rate at which the VOC is absorbed from the gas to the liquid phase. Poor solubility slows this mass transfer and reduces the viability of oxidation.

### Operating conditions

A number of factors need to be considered when operating biological techniques:

- the water content of biological systems is critical. Gas streams at temperatures above ambient will tend to cause water to evaporate, so careful checks will need to be maintained on water levels in the system. Traditional substrates based on peat or

heather have required a large amount of water, newer substrates based on activated carbon have lower requirements, are easier to manage and produce less effluent;

- biological systems are susceptible to inhibition, particle blinding and excess temperature, all of which can reduce the effectiveness of the biological population in the system. Inhibition may be caused by certain toxic gases (hydrogen sulphide, carbon monoxide), acid gases, heavy metals and high concentrations of cyanide (BMB 1998);
- systems usually need a fairly constant throughput (in terms of both flow and concentration), although recent innovations have seen the introduction of activated carbon substrates that can buffer the microbiological community against sudden 'spikes' in concentration;
- the choice of substrate to support the microbiological community is very important;
- biological systems can be particularly effective with large volumes of gas containing low concentrations of VOC;
- systems can be 'switched off' between batches without any adverse impact. However, for longer downtimes, typically 1-2 weeks, an artificial feed may have to be dosed to the system to support the biological community;
- trials will be required before the installation of any system to identify the optimum microbiological community and operating conditions. Acclimatisation of the biological community to the specific gas stream will also be required prior to the use of the system for abatement purposes. The need for acclimatisation does reduce flexibility to a certain degree for processes that may produce batches that give rise to very different releases.

The BMB (1998) has summarised the optimal conditions for biological oxidation. The main points are:

- temperatures in the range 15-30 °C (above 35-40 °C biological oxidation may be possible but only with very expensive, specialist equipment);
- high moisture content;
- high oxygen content;
- plenty of nutrients (N, P, Fe);
- usually neutral pH;
- constant ionic strength;
- absence of toxic inhibitors.

## Conclusions

Biological oxidation techniques appear to have a number of advantages compared to other VOC destruction techniques; for example, the minimal formation of secondary pollutants. In particular, they are relatively cheap to install and operate. The introduction of bio-reactors may address one of the early problems with biological techniques i.e the relatively large size of the space needed to install the equipment.

Notwithstanding these advantages, biological systems are still at a relatively early stage in their development and complex gas streams with variable flows/concentrations or those containing potential inhibitors may not be amenable to this type of treatment.

### 6.1.9 Overall conclusions on VOC abatement

A wide variety of techniques are available for the control of VOCs. These control techniques can be broadly broken down into either recovery techniques (condensation, adsorption, absorption) or destructive techniques (thermal oxidation, biological oxidation).

All five types of technique have been widely demonstrated in the sector and given the diversity of the sector and its emissions none can be said to constitute a 'universal' BATNEEC. This complexity means that the selection of which technique to apply will always be a site specific one and in practice many sites may well use more than one type of technique to deal with their emissions.

Notwithstanding the site specific nature of the control techniques for VOCs it is apparent that a number of important improvements have taken place in their performance. These include:

- catalytic oxidation is now a more robust technique, less susceptible to problems associated with the poisoning of catalyst beds but there still appears to be some resistance to its use by companies whose product range may change significantly over the years;
- biological oxidation has developed rapidly as a control technique, although its use is still restricted to gas streams with a fairly constant flow containing VOCs that biodegrade relatively quickly. In addition, certain substances may harm the biological community;
- cryogenics allow much lower condensation temperatures to be achieved, broadening the range of VOCs that the technique can be applied to whilst improving removal efficiencies. However, the high operating costs of such systems means that their use can be rarely justified unless nitrogen is used on a site for other purposes;
- flameless thermal oxidisers appear to have a number of advantages compared to other thermal techniques. Secondary fuel requirements and the potential for the formation of secondary pollutants is much less than for thermal oxidation. In addition, they are more robust than catalytic oxidisers. They may be particularly amenable for dealing with the large fluctuations in flow rate and concentration that are characteristic of this batch based sector.

Refinements have also been made to adsorption and absorption techniques.

The USEPA has issued a Handbook on Control Technologies for Hazardous Air Pollutants (REF). Figure 6.1, taken from the Handbook, shows approximate percent reduction ranges for add-on equipment (abatement techniques). The figure suggests that in terms of the concentrations that they can deal with:

- thermal oxidation can achieve 99% removal rates for virtually any concentration and that it is the only technique that can readily deal with very low VOC concentrations (approx. 20 ppm);
- catalytic oxidation has a narrower concentration operating band and generally cannot achieve the destruction efficiencies of thermal oxidation;
- carbon adsorption has a relatively narrow band (5000-10 000 ppm) in which it can achieve very good (99%) removal rates;
- absorption also has a similar relatively narrow band for very good removal rates;
- condensation is particularly good for high concentrations (more than 10 000 ppm).

This summary figure does not cover biological oxidation, which will typically involve good removal rates at low inlet concentrations. This figure should be treated with some caution, inlet concentration is just one factor that influences the overall choice of abatement technique.

The Environmental Technology Best Practice Programme (ETBPP) has recently published a solvent recovery guide. Entitled 'Solvent Capture and Recovery in Practice: Industry Examples' (ETBPP 1997d) it provides a very useful overview of the respective merits of VOC control techniques. This summary is re-produced in Table 6.4 below.

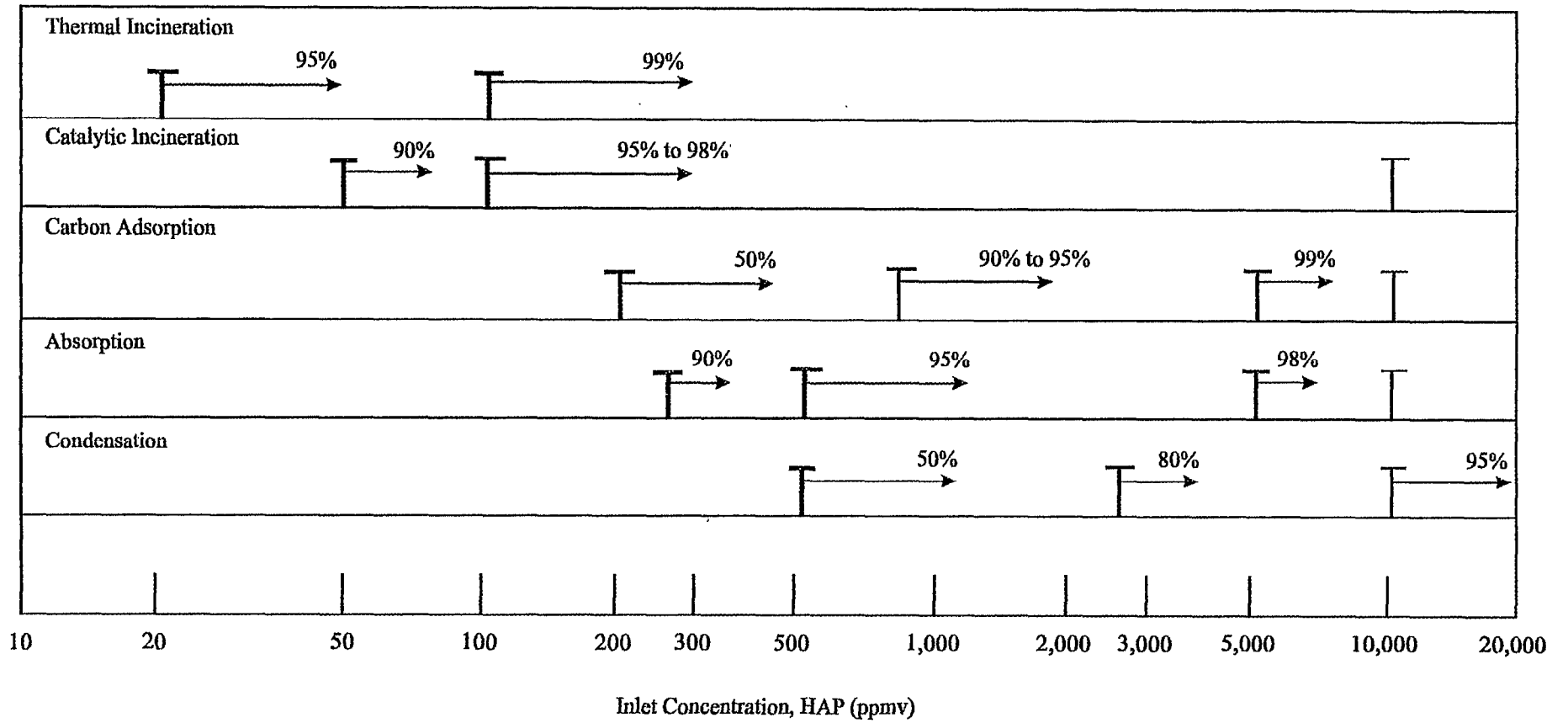


Figure 6.1 Approximate percent reduction ranges for add-on equipment (USEPA 1995)

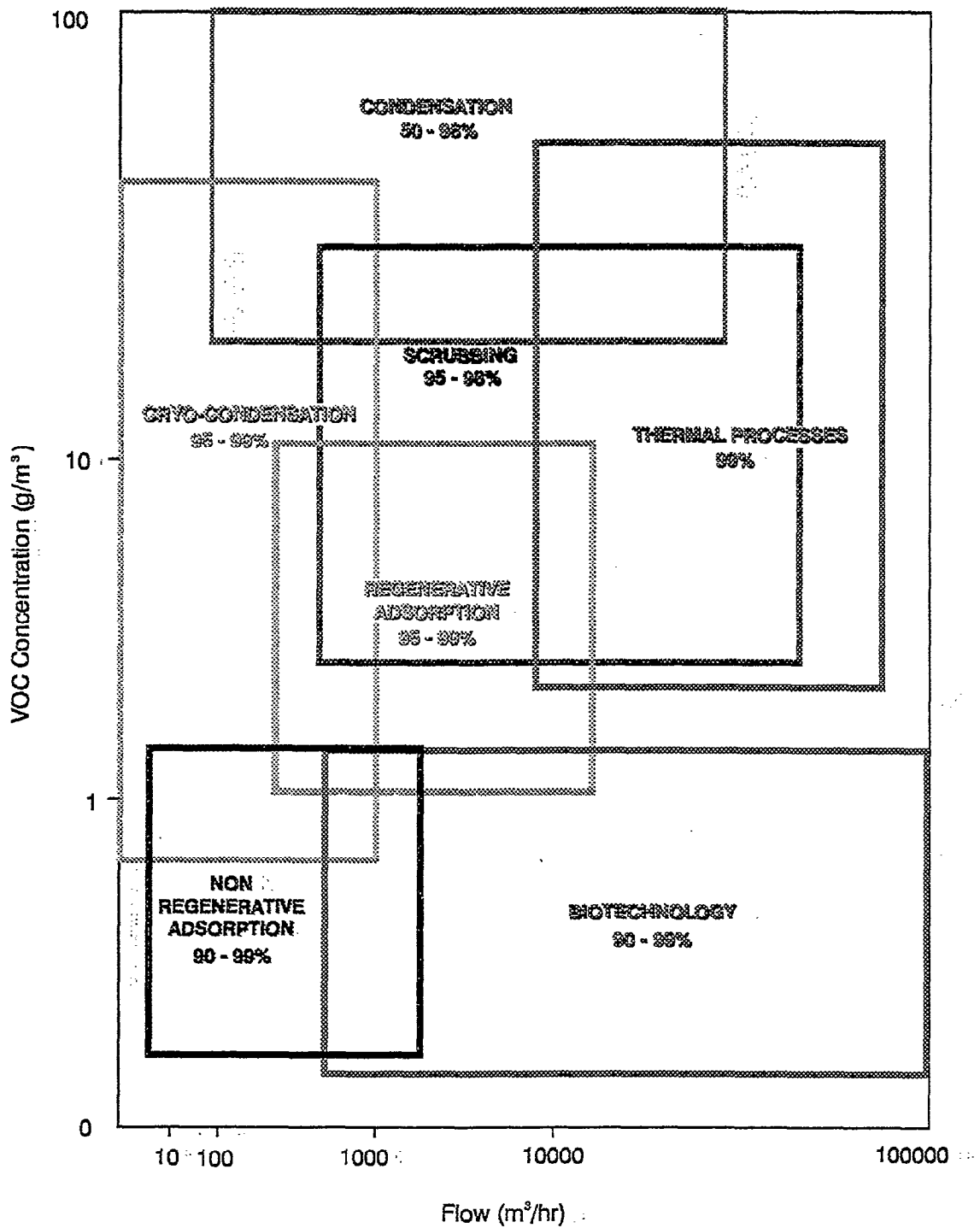


Figure 6.2. Flowrate and VOC concentration ranges applicable to VOC abatement techniques

**Table 6.4 Summary of the strengths and weaknesses of VOC control techniques**

Issue	Recovery and Re-use techniques			Destructive techniques		
	Adsorption	Condensation	Absorption	Thermal oxidation	Catalytic oxidation	Biological oxidation
Low flow/low concentration	A	B	A	B	D	A
High flow/low concentration	A	C	C	C	A	A
Low flow/high concentration	D	A	A	A	D	B-D
High flow/high concentration	D	A	B	A	D	E
Hydrocarbon gases	D	E	B-D	A	A	A-C
Halogenated or sulphated organic gases	D	E	A	B	D	C-E
Aminated organic gases	D	E	C-D	C	C	B-C
Hydrocarbon condensables	A	A	B-C	A	A	A-C
Halogenated or sulphated organic condensables	A	A	A-B	B	D	C-E
Aminated organic condensables	A	A	B	C	C	A-C
Continuous	A	A	A	A	A	A
Batch or variable	A	A	A	D	D	A
Removal efficiency	B	C	A	B	C	A
Pressure drop	C	B	B	A	C	A
VOC recovery	B	A	B	E	E	E

Key:

- A Excellent
- B Good
- C Satisfactory
- D Poor
- E Unacceptable



Table 6.4 suggests that for most scenarios at least one excellent recovery technique is available (the exceptions being for gas streams containing hydrocarbon gases and/or aminated organic gases). It would therefore appear that destructive techniques would have little applicability in the control of VOCs. However, in practice it should be remembered that there are further considerations not mentioned in Table 6.4 that are the key to deciding whether recovery/reuse techniques are feasible. These are the:

- number of VOCs present in the gas stream;
- presence of other contaminants such as particulates, moisture and acid gases;
- availability of an 'internal' or 'external' market for the recovered VOC.

If only one VOC is present in the gas stream then recycle should be relatively straightforward (provided the market availability test is passed) but as the number of VOCs present increases so does the complexity and cost of separating the recovered mixture into its constituent parts.

Similarly, the presence of other contaminants in the gas stream will have the effect of increasing the cost and complexity of recovery and will tend to make destructive techniques more favourable.

Once the feasibility of recovery has been ascertained attention needs to turn to the availability of a 'market' for the recovered VOC. Initially the availability of an 'internal' market needs to be considered. An 'internal' market is one the process operator can directly control i.e the recovered VOC be used in the originating process or some other process owned by the operator. Certain factors may mitigate against the availability of an 'internal' market, in particular purity considerations.

In the absence of an 'internal' market consideration needs to be given to the availability of an 'external' market into which that the process operator can sell or donate the recovered VOC. Although the 'external' market may offer a wide range of options, particularly relating to lower purity VOCs, this has to be balanced with the loss of control the process operator is likely to have. If the 'external' market cannot be guaranteed then the economics of recovery may be compromised.

### **Costs of VOC techniques**

Some approximate costs for various VOC abatement techniques are provided for indicative purposes in Table 6.5. Actual costs could differ widely from those quoted below. Costs, except where otherwise stated, include capital costs, civils and engineering costs.

The figures in Table 6.6 were provided by Sutcliffe Croftshaw (a manufacturer of abatement equipment). Again they relate to a hypothetical situation and should be considered to be no more than indicative of actual costs that may be incurred.

**Table 6.5 Some indicative costs for air abatement techniques**

Technique	Flow (m <sup>3</sup> /hr)	Conc	Approximate Capital cost £	Annual operating costs (£/year)	Annual operating costs (£/yr per m <sup>3</sup> /hr)	Includes	Does not include
Adsorption - Canister	200		1,000	100	0.5	Waste disposal	Indirect costs
Adsorption - regenerable fixed bed	10000	3000 g/m <sup>3</sup>	900,000	26,000	3	Two fixed beds of GAC Steam stripping Condensation Separation Decanting Steam, cooling water, electricity, labour, maintenance, carbon based on replacement every 5 years	Cooling De-humidifying Indirect costs Recovery credits (this is the balance between the costs of recycling/reusing - e.g further purification - and the cost savings associated with reduced solvent purchases)
Absorption	5000	20000 g/m <sup>3</sup>	550,000	17,000	3.4	Packed column Absorbent distributor Gas distributor Electricity, solvent (water - other solvents will change cost), labour, maintenance	Packed tower for steam stripping Condenser Decanter Pumps Heat exchanger Treatment of scrubber liquid Indirect costs Recovery credits
Condensation - refrigerant	1000	3000 g/m <sup>3</sup>	400,000	13,000	13	Shell and tube condenser Refrigeration unit Coolant brine solution Electricity, labour, maintenance	Pre-cooling Storage of recovered VOCs Refrigerant costs Indirect costs Recovery credits
Condensation - cryogenic			1,000,000	no data	no data		If liquid nitrogen or ammonia is already available on site then the costs may be reduced to £300,000

Technique	Flow (m <sup>3</sup> /hr)	Conc	Approximate Capital cost £	Annual operating costs (£/year)	Annual operating costs (£/yr per m <sup>3</sup> /hr)	Includes	Does not include
Thermal oxidiser	25500	20% O <sub>2</sub> 156 KJ/m <sup>3</sup>	1,000,000	278,000	10.9	Incinerator Stack Heat exchanger - 70% heat recovery Fuel, electricity, labour, maintenance	Flue gas scrubber could add another £500,000 to the cost. Treatment of the waste water from the scrubber would have additional cost implications Indirect costs
Catalytic oxidiser	34000	20% O <sub>2</sub> 80 KJ/m <sup>3</sup>	1,000,000	300000	8.8	Incinerator Stack Catalyst (costs vary from £15,000 to £65,000 per m <sup>3</sup> ) Heat exchanger - 70% heat recovery Fuel, electricity, labour, maintenance	Replacement catalyst. The cost of catalyst and the time period for replacement is highly variable. A rough rule of thumb would be 1m <sup>3</sup> of catalyst is required per 10,000 m <sup>3</sup> of gas treated. Catalyst costs approx £50,000/m <sup>3</sup> and requires replacement every three years. Flue gas treatment. Indirect costs
Biological oxidiser	3600	<500 mg/m <sup>3</sup>	300,000	5000	1.4	Concrete construction Humidifier Bio-filter	Blower Indirect costs

**Table 6.6 Indicative capital and operating costs for some hypothetical situations**

Plant	Solvent load (kg/hr)	Solvent group	Air flow (m <sup>3</sup> /hr)	Capital costs per m <sup>3</sup> of flow	Operating costs per year	Plant type	Capital cost
A	2600	Hydrocarbon	200350	£12.48	£620000	Adsorption with solvent recovery	£2500000
B	250	Alcohol	18700	£21.65	£50000	Adsorption with solvent recovery	£400000
C	226	Organohalogen/ alcohol	5000	£78.80	£108000	Adsorption with solvent recovery	£400000
D	2	Aldehyde/ alcohol	15000	£8.00	£12000	Bioreactor	£120000
E	20	Ketone/ ester	30000	£6.67	£24000	Bioscrubber	£200000

A comparison of Plants B and C show the potentially significant impact on costs of dealing with a mixed VOC gas stream with an adsorption technique. Operating costs are nearly doubled for Plant C, yet the flow and load it handles are less than those of Plant B.

The capital costs per m<sup>3</sup> of flow for the three adsorption techniques suggests some economy of scale for capital but not operating costs.

Both the capital and operating costs for biotechnology appears to be significantly lower than those for the adsorption techniques, although they offer no potential for recovery.

## 6.2 Control of Particulates

The control of particulates in the chemical industry is a well understood area of abatement and there has been little recent innovation. In addition, releases of particulates from this sector are generally less of a problem than are releases of VOCs. In this sense HMIP's 1994 Technical Guidance Note (A3) (HMSO 1994a) on pollution abatement technology for particulate removal can be said to be still the primary source of information.

The main techniques that are available for the control of particulates are;

- scrubbing;
- cyclones;
- filters; and
- electrostatic precipitators.

### 6.2.1 Scrubbing

Scrubbing is the only technique that can be used to remove volatile organic compounds (VOCs; see Section 6.1) and particulates but not generally at the same time. Scrubbing operates on the principle that particulates can be removed from the gas stream by dissipating their momentum. This dissipation can be achieved either by impacting particulate on to the scrubbing liquid or impacting a solid surface which is then washed with the scrubbing liquid.

Scrubbing to remove particulates does not require as much care in the selection of the scrubbing liquid as does removal of VOCs but the main delivery systems for contacting the scrubbing liquid with the gas stream are broadly similar and are summarised in Table 6.7.

**Table 6.7 Mechanisms for contacting the scrubbing liquid with the gas stream**

Technique	Principle of operation	Potential constraints
Packed tower	The gas stream is passed through fibrous mats irrigated with the scrubbing liquid	Insoluble particles may accumulate and block the mats
Plate tower	The gas stream is passed upwards through a number of perforated plates. The plates have baffles above the perforations to slow the gas. The plates are constantly wet with the scrubbing liquid.	The perforations may become blocked
Spray tower	The gas stream is passed up a tower. The scrubbing liquid is introduced to the tower via nozzles at the top or along the sides of the tower	The spray nozzles may become blocked
Venturi tower	The gas stream is used to atomise the scrubbing liquid into droplets and is then accelerated through a venturi throat. Mixing of the scrubbing liquid droplets and the gas stream occurs as they leave the throat	At very high velocities, erosion of the venturi throat may occur
Impingement	The gas stream is accelerated into a pool of the scrubbing liquid. Droplets containing particles are formed by the impact and are removed from the gas stream by an impingement plate	
Fluidised bed	The gas stream is used to suspend a mobile bed (often hollow plastic balls). The mobile bed is wetted with the scrubbing liquid	The mobile bed may deteriorate.

Scrubbing systems tend to be less effective than other alternatives for the control of particles <10 µm. They also generate an effluent that will require treatment.

## 6.2.2 Cyclones

Cyclones are widely used for the collection of particulates. They are particularly effective for the removal of particles with a diameter  $>10\ \mu\text{m}$  and are often used as a secondary device for the protection of more expensive abatement equipment that can achieve better release levels.

There are two basic types of cyclone:

- reverse flow; and
- straight through.

These are differentiated by the geometry with which the gas stream enters the cyclone. The design of a cyclone will depend upon the particular gas stream that is being dealt with. The following factors need to be taken into account during the design of a cyclone:

- density of particulates;
- inlet velocity;
- cyclone length;
- number of gas revolutions;
- ratio of body diameter: outlet diameter;
- particle diameter;
- amount of dust.

Although manufacturers continue to make minor improvements to cyclone removal efficiencies, this is a relatively mature abatement technique. Therefore no one approach can be said to be BATNEEC.

## 6.2.3 Filters

Filters are widely used for the collection of particulates  $>1\ \mu\text{m}$  and can usually achieve efficiencies of greater than 99%. The main variables that are available in designing filters are:

- the filter medium;
- the manner in which the filter is periodically cleaned.

### Filter mediums

A number of filter mediums are available to deal with a wide range of variables such as the temperature, corrosiveness, composition, particle size etc. The mostly commonly used filter medium is fabric. Table 6.8 summarises some of the more important fabrics that are used as filter mediums.

**Table 6.8 Materials utilised in fabric filters**

Common name	Generic name	Chemically resistant to		Operating temp (°C)	Max temp (°C)	Fire resistance
		Acids	Alkalis			
Cotton	Natural fibre cellulose	Poor	Excellent	80	105	Poor
Polypropylene	Polyolefin	Excellent	Excellent	87	87	Poor
Glass	Glass	Good	Poor	260	287	Good
Nylon	Polyamide	Poor	Excellent	93	121	Poor
Nomex	Aromatic polyamide	Fair	Very good	204	218	Poor
Teflon	Fluorocarbon	Excellent	Excellent	232	260	Poor
PBI	Polybenzimidazole	Good	Fair	537	649	Poor
Gortex	Polytetrafluoroethylene	Excellent	Excellent	230	260	Poor
Dralon T	Homopolymer acrylic	Good	Excellent	140		Poor
Bekipor	Stainless steel	Good	Good	454	538	Good

Table 6.8 shows the diversity of fabric filters that are available. They can cope with a wide range of substances and operating conditions but there are limitations to their use. Very high temperatures and large, instantaneous temperature changes are often most usefully dealt with by the use of ceramic cartridges. Moisture and sticky particles can also reduce the effectiveness of fabric filters.

The fabric used in the filter has been the main source of innovation in recent years in filter techniques. New materials have been developed that allow improved removal efficiencies under a wider variety of operating conditions.

### Cleaning mechanisms

As particles build up on the surface of the filter they initially aid the filtration mechanism but they eventually begin to reduce gas stream throughput and reduce the efficiency abatement. To address this problem fabric filters are fitted with cleaning mechanisms that allow the periodic removal of the build up of particles. There are three main mechanisms for this particle removal, which may be summarised as:

- pulse jet - whereby a pulse of compressed air is applied to the filter in the reverse direction to the normal flow of the gas stream;

- shaker - the bag is shaken;
- reverse flow - clean air is passed through the filter medium in the reverse direction to the normal flow of the gas stream.

### **Control of fabric filters**

The main issues involved in the control of fabric filters are:

- ensuring that procedures are in place to clean the filter before operating efficiency is compromised by excessive build up of captured particulates. This will usually be based on the measurement of pressure drop across the system. Additionally, an opacity monitor may be used to identify bag failure;
- managing the operating temperature of the gas stream. If the temperature is too high the filter may be damaged, if it is too low moisture may condense out of the gas stream making the captured particles sticky and eventually causing blinding of the filter;
- the risk of fire caused by particles that are particularly hot (unlikely in the chemical industry) or explosion from explosive dusts. When there is the potential for the latter to occur some kind of explosion relief mechanism should be available.

#### **6.2.4 Electrostatic precipitators**

Electrostatic precipitators use an electrostatic field to charge the particles in a gas stream. The charged particles are then attracted to a grounded surface from which they are periodically dislodged into a collection system.

Because of the risks of fire and explosion associated with their use, electrostatic precipitators are not widely applied in the chemical industry.

#### **6.2.5 Overall conclusions on particulate abatement**

The main advantage of fabric filtration is that it is not an efficiency device i.e it provides a relatively consistent exhaust concentration irrespective of the inlet load. However, efficiency drops off in the presence of moisture, sticky or corrosive material and this is when wet scrubbing systems may be particularly effective.



## **7. WASTE WATER MANAGEMENT**

### **7.1 Introduction**

Guidance has already been issued by the Environment Agency on the treatment of waste water from IPC processes (HMSO 1996c). This section concentrates on the specific requirements of the sector.

Because the sector is characterised by an extensive range of products and process chemistries it is not uncommon to find sites where significant changes in production methods and products occur within a short period of time. Consequently the associated waste waters may change in volume and composition. This variability has to be taken into account in the selection of techniques for waste water management.

Waste water arising from this sector can only be treated effectively and efficiently if its source, composition and volume are understood. These issues are addressed in the first part of this section before a consideration of the individual techniques that can be applied.

There are four broad sources of waste water in the sector. These are:

- cleaning of process equipment;
- water use as part of the synthetic process - as a solvent, reagent etc;
- water as a heat transfer agent; and
- run off water from the site.

In general terms the better the separation of waste water from these four sources the easier will be its subsequent management.

This section considers the treatment of waste water in the following manner:

- identifying and defining waste water problems;
- understanding water use by the process and, if relevant, wider site;
- addressing these problems by selecting appropriate abatement techniques, which may include:
  - special treatment of segregated streams;
  - pre-treatment prior to central treatment;
  - central treatment;
  - polishing after an earlier treatment stage.

### **7.2 Identification and definition of waste water issues**

A process operator may be expected to first identify and define all waste water issues involved with a process. This may be expected to include the:

- identification of process and site specific issues;
- characterisation of all waste water streams;
- characterisation of minimum water quality and quantity requirements for the process;
- identification of opportunities for waste stream modification.

Figure 7.1 provides an overview of these issues and they are discussed in more detail below.

### **7.2.1 Process and site specific issues**

Any consideration of waste water management issues for a process should be built on certain basic information. This includes:

- working diagrams of the total site showing location of main process units, buildings, treatment plant and any pre-treatment;
- drainage plans of the site for foul, process and surface water drainage systems showing sewer connections and the main entry and outfall points;
- diagram of water supply and water treatment systems showing the positions of any meters and storage reservoirs;
- map showing the aquatic environment in the proximity of the process e.g surface water systems, groundwaters and sewers.

There is an increasing trend for sites to be occupied by more than one process operator. Particular attention should be paid on these sites to ensuring that responsibilities are clearly delineated on all maps and diagrams.

### **7.2.2 Characterisation of all waste streams**

One of the major difficulties with waste waters arising in this sector is that of identifying the chemical constituents and their properties in relation to technique performance. This also applies to quantity aspects and is generally referred to as characterisation of the waste streams. In general, characterisation of waste streams should include:

- flow monitoring of the main process effluent flows;
- pH and temperature logging;
- sampling of the main combined process effluent streams and individual (segregated) process effluents known to be a potential problem and analysis for a number of determinants. These should include BOD, COD, suspended solids, ammonia, and possibly specific compounds relevant to the processes operated and/or likely effluent consents. Effluent toxicity may also have to be considered if biological treatment is an option or there are reasons to expect toxic effects from the discharge of the effluent;

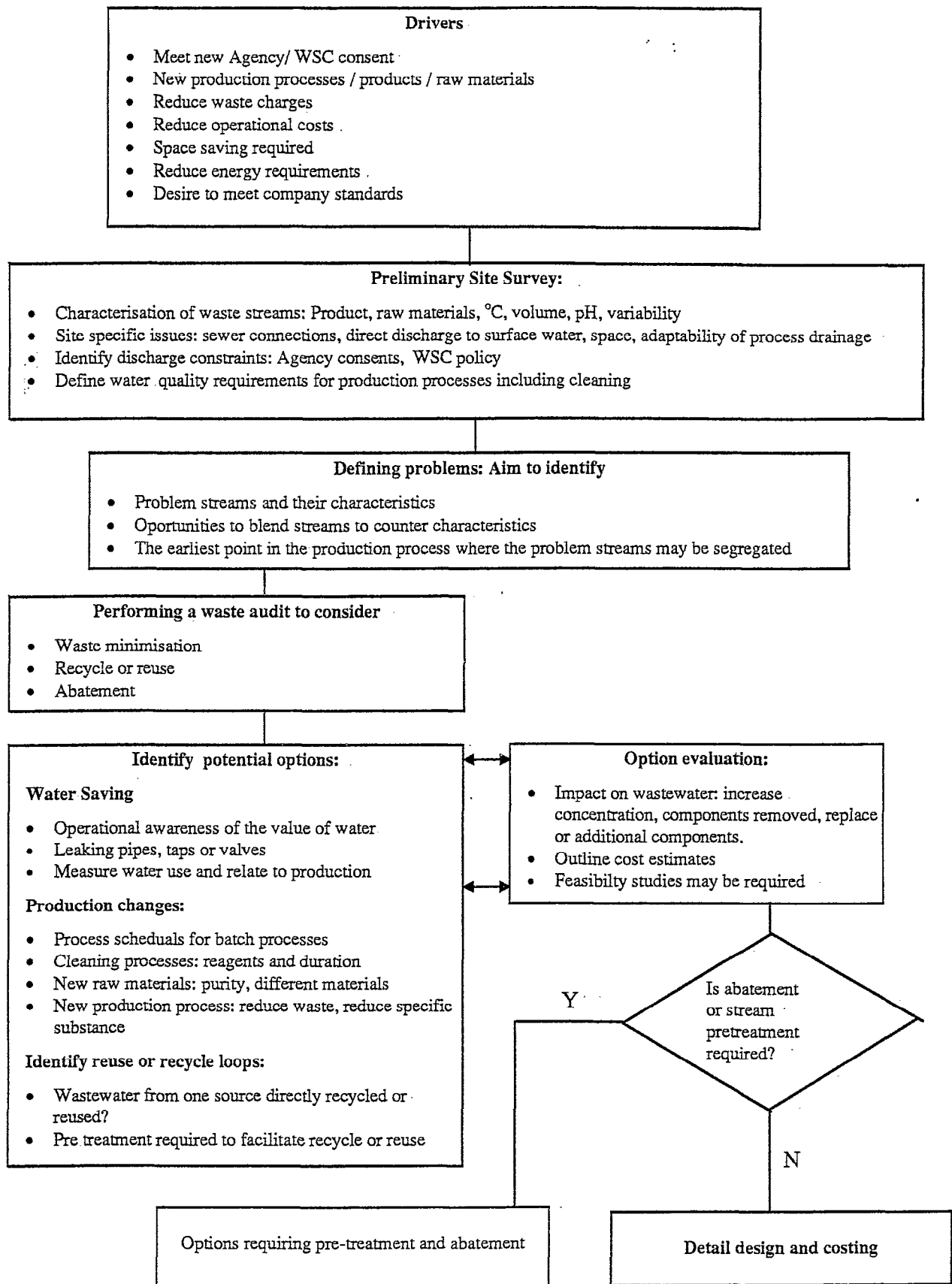


Figure 7.1 Identifying and defining waste water issues

- a list of chemicals used, potential contaminants and mass balances for the production processes will also be of value in terms of identifying potential problems that may arise under non-routine conditions;
- derivation of the potential 'worst case' combination flow and loads under routine and non-routine conditions;
- assessment of the impact of likely future production changes on the measured effluent flows and loads.

### **7.2.3 Define water quality and quantity requirements for production processes**

The water required for different parts of the production and cleaning process should be defined in terms of quality and quantity to enable reuse and recycling issues to be addressed.

### **7.2.4 Identify opportunities for waste stream modification**

Identification of the major sources of waste water offer opportunities for reducing overall discharges, by for example, changes in production practices or the introduction of special treatment of segregated streams. In particular waste streams can be modified by blending or segregation to improve subsequent treatment.

#### **(a) Blending**

Typically blending may include pH balancing and the dilution of very strong streams to facilitate a downstream abatement process.

#### **(b) Stream Segregation**

Issues of compatibility between all the components of the streams to be mixed need to be reviewed to assess the need for segregation. Streams that are not amenable to mixing will have to be treated and/or disposed of separately. Potential segregation issues include:

- pH will affect the solubilisation of metals and some organics. It may reduce the amenability to biological treatment or may make the combined stream more corrosive than it was formally;
- temperature increases could facilitate the liberation of solvents or sulphides and may also cause an increase in reactions between chemicals whilst they are in the pipes;
- reactions between the chemical constituents must also be considered;
- solids may clog up adsorbents and filters;
- in oxidation systems the oxidising agent may actually be used up on other organic components rather than those of most concern.

(c) Treatment of segregated streams :

Once the need to segregate has been identified the options for treating the segregated stream need to be considered. The value of treating individual streams is now widely recognised and Figure 7.2 identifies some of the potential options for special, single stream treatment. This figure is purely indicative of the wide range of options that are available; many more combinations can be used to deal with specific problems. Further information on special treatment techniques is provided in Section 7.5.

### 7.3 Water use

Water use, waste water generation and subsequent treatment are intrinsically linked. The process operator should not consider these issues in isolation from each other and should in practice assign them an equal weighting.

The Environmental Technology Best Practice Programme (ETBPP) has issued a best practice guide on water use in the speciality organic chemical sector and this should be referred to for more information (ETBPP 1997e). This guide notes the very wide variation in water use and waste water discharged per tonne of production. Notwithstanding this it makes an attempt to assign various products typical of the sector to ranges of water use/waste water discharged per tonne of production and these are repeated in Tables 7.1 and 7.2, respectively.

**Table 7.1 Water consumption per tonne of production**

Specific water consumption (m <sup>3</sup> /tonne production)						
less than 1	1-2	2-5	5-10	10-50	50-100	100+
Resins	Sulphonic acids	Silicones	Brightening agents	Esters	Pharmaceutical intermediates	Liquid crystals
Adhesives	Detergents	Polyacrylics	Dyes	Biocides	Acrylates	Buffer solutions
Detergents	Rubbers	Water treatment chemicals	Biocides	Fungicide intermediate	Amine products	Pigments
Disinfectants	Resins	Chelating agents	Herbicides	Mercaptan gas		Chlorine and bromine products
photographic solutions	Pigments	Surfactants	Insecticides	Odorants		
betaines	Salts	Amine products	Phosphates	Carbonates		
		Synthetic organic polymers	Pharmaceutical intermediates	Thioglycollate s		
		Sulphonic acids	Polyacrylics	Thioureas		
		Esters	Amine products			
		Imides	Esters			
		Anhydrides	Soaps			
		Quaternaries				
		Alkyl ethers				
		Salts				
		Soaps				

**Table 7.2 Waste water discharge per tonne of production**

Specific waste water discharge (m <sup>3</sup> /tonne production)					
less than 1	1-5	5-20	20-50	50-100	100+
Soaps	Water treatment chemicals	Brightening agents	Salts	Acrylates	Liquid crystals
Sulphonic acids	Surfactants	Dyes	Esters	Amine products	Buffer solutions
Salts	Amine products	Esters	Imides		Pigments
Acrylates	Polyacrylics	Betaines	Anhydrides		Chlorine and bromine products
Detergents	Chelating agents	Biocides	Dyes		
Disinfectants	Synthetic organic polymers	Fungicide intermediates	Biocides	Pharmaceutical intermediates	
Photographic solutions	Acrylates	Rubbers	Herbicides		
Resins	Herbicides	Resins	Insecticides		
Adhesives	Phosphates				
Pigments	Esters				
	Sulphonic acids				
	Silicones				

### 7.3.1 Water savings

The overall company approach to water use on-site is of the utmost importance if process water use is to be minimised.

Typical techniques for reducing water use are:

- management practices such as water use targets, audits and water use:product ratios may be appropriate;
- the use of closed loop cooling systems;
- the recycling of used 'clean' wash waters for dirty equipment wash down;
- process changes to reduce the use of water intensive equipment;
- metering of each process and, where water use is significant, individual process units;
- substitution of wash water by solvent wash with the solvent being subsequently reused;
- regular checks of taps, pipes and valves for leaks, and maintenance where required;
- awareness raising and training for staff.

### 7.3.2 Production changes

Changes in the production process may enable reductions to be made in water use. For example, it may be possible to replace stages which require excessive cooling with alternative approaches. Section 5 on Process Techniques provides more information in this area.

### 7.3.3 Reuse or recycle

The reuse (the use of water for the same or some other purpose) and recycle (the use of water for the same purpose) of water offer significant opportunities for minimising water use but their use should not be indiscriminate and their potential to cause problems should not be overlooked.

In some cases the minimisation or reuse and recycling of wastewaters will require no new technology to achieve the desired objectives. In this case modification to process plant may be the only option being evaluated.

When considering the potential options for reuse/recycling attention should be paid to the potential implications for waste water quality. Water savings may reduce the volume of effluent but the concentrations of chemicals may increase correspondingly. The effects of such increased concentrations may include:

- problems with downstream processing;
- potential for pipe blocking;
- the increased blocking of filters resulting in more frequent replacement or backwashing;
- overload of treatment systems causing contamination or inadequate control efficiencies;
- tainting of products;
- change in the odour potential;
- increased corrosiveness;
- increased dissolved solids content.

For this reason a test regime may be required to monitor the water quality within reuse/recycle loops to ensure that the water remains fit for the purpose. When implementing test regimes consideration needs to be given to:

- ensuring that the costs of monitoring are included in the evaluation stages;
- the potential options for treating the concentrated waste water or its disposal requirements;
- the additional water requirement if dilution is subsequently used to reduce the concentrations of contaminants;
- the options for in-loop treatment and the associated disposal requirements of waste contaminants;
- the assessment of the potential health and safety issues resulting from failure of treatment.

## 7.4 Abatement Technique Selection

Once the characteristics of the waste water have been identified consideration will need to be given to the options for treating (abating) it. There are four potential stages in waste water treatment:

- special treatment of segregated waste water streams;

- pre-treatment prior to central treatment;
- central treatment;
- polishing treatment after an earlier treatment stage.

In practice processes will often combine two or more of these stages. The combination adopted will be process specific and will reflect considerations such as waste water characteristics and the receiving medium (i.e sewer or surface water). Figures 7.2 (adapted from Mann 1991) and 7.3, respectively, illustrate the potential interactions between the four stages. Certain techniques may be applied at either the special or polishing stages.

Regardless of the waste water to be treated or the technique finally selected there are certain requirements that must be achieved. In a selection procedure consideration of these minimum requirements will help screen the options to identify the few that merit detailed consideration. Examples of such requirements include:

- meets the objectives identified (e.g in terms of meeting existing and potential future consent conditions);
- has sufficient mechanical and operational reliability;
- allows adequate containment of waste streams;
- causes the cross media transfer of pollutants e.g emissions of VOCs to air from holding and treatment tanks, the disposal of treatment sludges to landfill, incinerator or land;
- protects any sewerage system and sewage treatment works that may subsequently receive the waste water;
- ensures that no adverse impact is caused by downstream combined sewer overflows;
- minimises secondary environmental impacts such as noise, odour, visual impairment and access by service vehicles;
- minimises the risk of accidents;
- requires a minimum space;
- entails excessive capital or operating costs;
- minimises energy consumption;
- has a sufficient degree of automation and control.

Some criteria may be considered as desirable qualities rather than absolute requirements. For example degree of automation and certain secondary environmental impacts. The relative importance of the selection criteria will be site specific. Where possible absolute constraints should be recognised, for example the maximum space that is available. The theoretical options can then be considered against these criteria and compared and contrasted with each other.

On the basis of these comparisons a short list of options will probably be identified. Pilot trials or evaluation studies may then be performed to provide data for the final selection. It might be reasonable to expect that the selection procedure is documented for future reference.



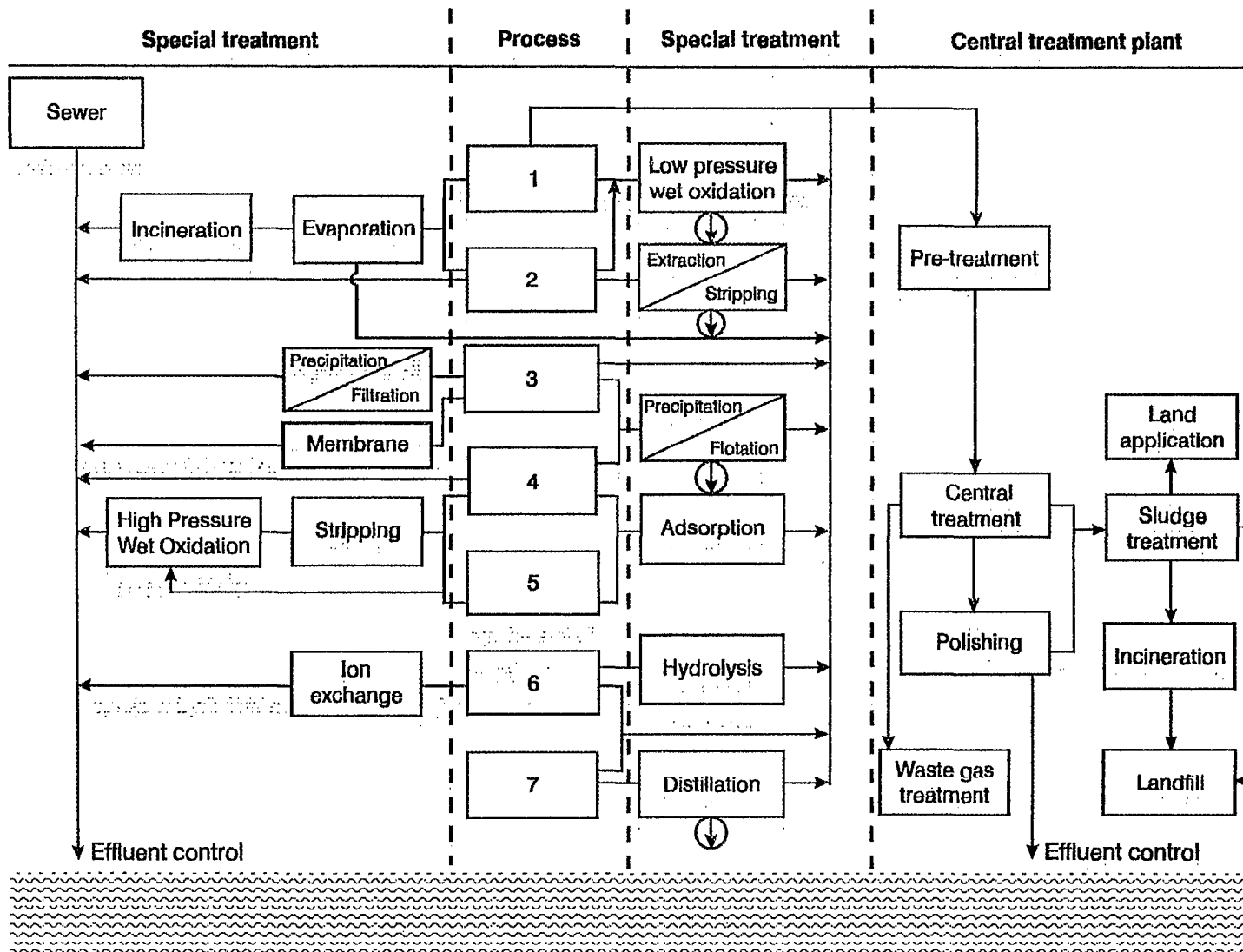


Figure 7.2 Potential special and pre-treatment waste water techniques

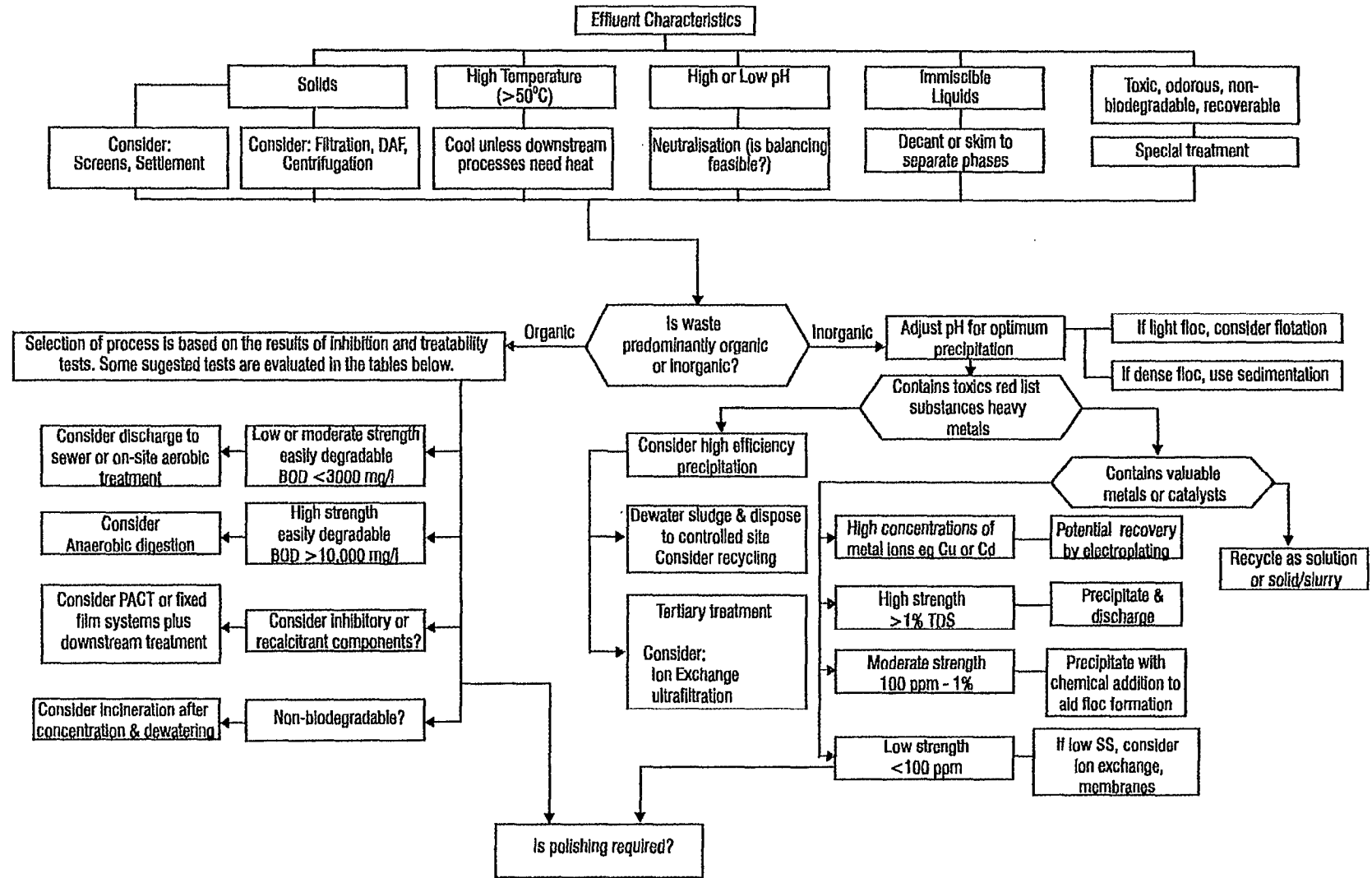


Figure 7.3 Decision tree for identifying waste water techniques

Table 7.3 lists the types of abatement technique which may be used to deal with specific families of contaminants. The contaminants have been listed in the order in which they are most likely to be considered for removal. Factors that may determine the order of treatment are:

- is the contaminant likely to interfere with down stream processes;
- the cost effectiveness of removing the contaminant prior to subsequent steps. This may be in terms of energy or in the increased size and capital costs of down stream processes.

**Table 7.3 Techniques used to remove major contaminants found in wastewater**

Contaminant	Abatement technique
Suspended solids	Sedimentation Filtration Flotation Chemical polymer addition Coagulation/sedimentation
pH	Neutralisation
Insoluble organics	Separators
Volatile organics	Air stripping Steam stripping Activated carbon Evaporation Distillation
Biodegradable organic	Aerobic Anaerobic
Metals	Chemical coagulation
Nutrients (N)	Suspended-growth nitrification and denitrification variations Fixed-film nitrification and denitrification variations Ammonia stripping Ion exchange Breakpoint chlorination Natural systems
Nutrients (P)	Metal-salt addition Lime coagulation-sedimentation Biological phosphorus removal Biological-chemical phosphorus removal
Nutrients (N+P)	Biological nutrient removal
Refractory organics	Carbon adsorption Ozonation Supercritical water oxidation Wet air oxidation Chemical oxidation
Dissolved organic solids	Ion exchange Membranes

Figure 7.3 shows a flow diagram depicting the decision or factors that most significantly influence the abatement technique selected. It is reasonable to expect the company to demonstrate to themselves and to the inspector that the selected abatement technique will perform the desired task.

## **7.5 Special Treatment**

Special treatment techniques are generally applied to specific waste streams that cannot be discharged to central treatment or to sewer without first being treated or modified in some way. A number of special techniques are available and these include:

- air stripping;
- steam stripping;
- distillation;
- wet air oxidation;
- super critical water oxidation;
- chemical oxidation.

Solvents are used extensively in the sector and special treatment is often applied to recover or treat them. The feasibility and extent of recovery and subsequent reuse/recycle are governed largely by the quantities involved and by the complexity of solvent mixtures to be separated. If reuse/recycle is not economically practicable, the recovered solvents may have to be disposed of by means of incineration, landfilling, contract disposal etc.

Even when an effort is made to recover solvents, some waste water contamination can be expected. Removal of small quantities of organic solvents from the segregated waste water can be accomplished by such techniques as steam or air stripping. Further removal of solvents from combined end-of-pipe waste water may result from biological treatment or from surface evaporation in the treatment process. The potential for VOC emissions during the treatment process should be considered by the process operator.

For waste waters that are not amenable to recovery, some kind of destructive technique will have to be applied. These techniques are usually based on some form of oxidation.

### **7.5.1 Air Stripping**

The close contacting of the water with a current of air enables volatile compounds in the water to evaporate. Aeration/air stripping covers various ways of carrying this out. The most common methods used are:

- packed tower aeration - waste water is passed downwards through a tower filled with a packing material designed to maximise the contact with air which is blown up through the tower;
- spray aeration - waste water is ejected as a fine spray through nozzles into a collector;

- diffused - air is sparged or bubbled through the water, the aim being to minimise the size of the bubbles in order to maximise the contact between water and air.

Air stripping is only suitable for the removal of volatile compounds from waste streams, although the temperature of the air can be increased to drive off less volatile components. It also removes dissolved carbon dioxide from the water, thus increasing the pH and also, in hard waters, increasing the possibility of scaling of the equipment. The technique is likely to be more cost effective than adsorption at high concentrations.

There will be an energy cost associated with air stripping. This will be related to the pumping costs for spray aeration or for feeding a packed tower, and the air blower/compressor power consumption for packed tower and bubble aeration.

The compounds which are removed by air stripping may require abatement (see Section 6.1) or collection for disposal via some other route e.g incineration. The actual final disposal route will depend on the VOCs involved.

Air stripping performance data for a number of VOCs are summarised in Table 7.4.

**Table 7.4 Stripping performance data for a number of VOCs**

Compound	Aeration	%	Air:Water
Carbon tetrachloride	PT	90 to 98	5 to 35:1
1,2-dichloroethane	PT	65	35:1
trichloroethylene	PT	69 to 92	4 to 30:1
	Sp	90	
perchloroethylene	PT	95	5:1
	Sp	90	

Notes: PT: packed tower, Sp: Spray aeration

### Costs of air stripping

These cost functions were derived for Q3 1997, and relate to a packed tower of height 3 metre, using an air velocity of 1m/s (WRc 1977).

#### (a) Capital costs

TOWER (£'000)	$4.3 \times (\text{ATW} \times \text{FLOW})^{0.4}$
BLOWER (£'000)	$5.9 + (\text{ATW} \times \text{FLOW} / 147)$
PACKING (£'000)	$\text{PACKCOST} \times \text{ATW} \times \text{FLOW} / 28,8000$
ATW	Air:Water Ratio
PACKCOST	cost of packing (£/m <sup>3</sup> )
FLOW	Ml/day

## (b) Operating costs

BLOWER POWER COST (£'000/year)       $ATW \times FLOW \times ECOST / 655$   
ECOST      electricity cost (p/kWh)

### 7.5.2 Steam Stripping

Steam stripping is not as widely applied as air stripping to remove VOCs. Its larger energy requirements are generally not required to remove most VOCs and its use is usually confined to removing less volatile components that are soluble in water, for example acetone and methanol.

Steam stripping usually utilises a column, often containing a packing or trays to improve separation. The separated waste water and organic compound(s) can be collected in a gravity separation tank. The ease with which the organic compound can be separated from the condensed water will thus be a factor. If a column is used consideration may need to be given to the fitting of an air abatement technique to prevent losses to atmosphere.

Steam stripping can also be used to remove ammonia from waste water. Influent waste ammonia liquor is pumped through a feed pre-heater to recover heat from the stripped effluent and enters a column containing bubble-cap trays. Caustic soda is added to maintain the pH above 9.5 so that ammonia is free to be stripped. Low pressure steam is introduced into the bottom of the column and passes up through the bubble-cap trays counter-currently to the flow of waste water. The mixture of stripped ammonia and steam leaving the top of the column passes through an air or cooling water condenser to produce condensate which is returned to the top tray. Uncondensed vapour from the condenser contains about 25 to 30% ammonia by weight and is transferred to either an absorber to produce an ammonia liquor stream or to an incinerator.

Steam stripping typically removes about 99% of the ammonia from a waste stream reducing the ammonia concentration present in the influent from about 1% by weight to less than 50 ppm. The process has a steam usage of about 0.3 tonne steam/tonne of effluent treated. It produces a waste steam containing ammonia at a concentration of about 25% by weight. Any volatile components present in the waste stream will also be stripped out into the steam.

Treating the waste steam in a absorber recovers a saturated 25% by weight ammonia liquor stream which may be acceptable for re-use in the existing production processes at the site. Alternatively it may be suitable for use in fertiliser manufacture.

If the waste ammonia stream is incinerated, the off gases will contain  $NO_x$  and need treatment in suitable air pollution control equipment. If the original waste stream contained halogenated or sulphurous compounds, these components will be stripped into the steam and require additional air abatement techniques.

### 7.5.3 Distillation

Mainly because of the cost of the energy requirements, treatment of waste water by distillation is not widespread. The only hazardous waste materials which can be feasibly and practicably

treated are liquid organics, including organic solvents and halogenated organics, which do not contain appreciable quantities of materials that would cause operational or equipment problems.

### Energy and economics

The difficulty in separating the constituents of the liquid mixture to be distilled defines the energy requirements and associated operational costs. The difficulty of separation is dependent on a number of things, including the:

- concentration of the waste water's constituents;
- degree of separation desired;
- relative volatility of the constituents in the feed;
- existence of contaminants.

Capital investment is also affected since for higher product purity, larger size equipment is required and perhaps more sophisticated instrumentation.

For any binary distillation, there is an infinite number of design possibilities ranging between minimum reflux with an infinite number of stages on one hand, and minimum stages and total reflux on the other. From an economic standpoint, the optimum design is one that achieves the desired goal at the lowest cost. Because both capital and operating costs are involved, a relationship must be established between them. Furthermore, since the particular relationship employed varies from company to company and from process to process, no single relationship between the two costs can be specified.

As the amount of liquid refluxed is increased, more energy is required for condensation and ultimate revaporisation, thus escalating operating cost, but the number of stages is reduced, and this reduction lowers the investment required over the range of reflux ratio normally considered. There is one exception to this rule; at higher-than-normally-used reflux ratios, the increasing reflux ratio increases the diameter of the column and the size of all auxiliaries, and reduces the number of required stages, under these circumstances, investment costs would increase, with increasing reflux ratio. Thus, the optimum design consists of balancing one cost against the other to obtain a minimum cost. At low reflux ratios, the calculated separation is sensitive to small operating changes and to relative volatility.

Heat may be supplied to a distillation column by pre-heating the feed or by reboiling the bottom product. In general, pre-heating of the feed should be minimised and reboiling heat maximised; since heat supplied to a pre-heater provides vapour only to the rectifying section, whereas reboiling heat is also effective in the stripping section. Sometimes, however, adding all the heat in the reboiler may make the column unbalanced with regard to vapour rates, the stripping vapour rates becoming larger than the rectifying rates; and then a larger diameter column may be required. In this latter case, pre-heating the feed would be a practical solution.

Other items which may affect the heat requirements for a column are whether or not it is indoors or outdoors, what the prevalent ambient conditions are, and whether or not the column and associated equipment are insulated.

Because of all of the variables which affect the capital investment and operating cost and the energy requirements for any particular distillation, there is no such thing as a typical cost for distillation on a unit product or on a unit feed basis. This becomes even more evident when all of the different organic liquids and the range of possible concentrations and the feed conditions (i.e. temperature, whether or not there are contaminants, etc.), are taken into consideration.

Still bottoms may present a waste disposal problem, since they sometimes contain considerable quantities of tars and sludges and these are usually incinerated. Vacuum distillation using steam or water eductors, yields volatile impurities in the condensed steam or water used to produce the vacuum. Disposal of this waste water is always a problem. Where disposal or treatment of this waste water is a major problem, mechanical vacuum pumps might be considered as an alternative to the eductor.

The Environmental Technology Best Practice Programme (ETBPP) has recently initiated research into improving the energy efficiency of distillation operations. This is likely to result in the issuing of guidance in 1998 (Morrell 1997).

### **Alternative approaches**

It may be more economical for those who generate relatively small volumes of solvent effluents to pay a contractor to haul the waste stream away; have them recover the solvent and then buy it back. Total cost to the client for recovery of solvent may represent a saving of 13-20% over the solvent market value. The solvent reclaimer, on the other hand, makes about a 10% profit, since he normally has a much lower capital recovery charge than would the process operator. This is because:

- capital investment may be lower - for used equipment, or old equipment which has already been written off; or
- better overall utility of the equipment can be made, thus imposing lower capital cost application for each particular waste stream handled.

#### **7.5.4 Wet Air Oxidation (WAO)**

Wet air oxidation involves the oxidation of aqueous wastes (organic and inorganic) at temperatures in the range of 177 to 315 °C and pressures between 7 to 200 bar. The feed stream is pre-heated by heat exchange with hot oxidised effluent. Waste water and oxygen or air are continuously fed into the reactor by high pressure pumps.

The degree of oxidation is dependent on the temperature and residence time and the chemical substances present. The combustion process is autothermal at COD values greater than around 10 000 mg l<sup>-1</sup>, and waste waters with greater than 100 000 mg l<sup>-1</sup> COD can be handled if diluted. Therefore the typical application is for characteristically high COD wastes which are not biodegradable and which are not concentrated enough to incinerate. It may also be used for the treatment of sludges from biological treatment plants and for the regeneration of powdered activated carbon (PAC).



Organic compounds are oxidised, in varying proportions, to CO<sub>2</sub>, H<sub>2</sub>O and simple oxygenated organic acids and aldehydes. The residual acids may be treated by a further biological treatment stage. They may also be vented to air and appropriate air abatement techniques may have to be applied. Halogenated organics are dehalogenated giving the halogen ion (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>). Sulphur is converted to the sulphate ion.

Data supplied for the removal of a number of pesticides by wet air oxidation is provided in Table 7.5.

**Table 7.5. Wet air oxidation removal efficiencies for a number of pesticides.**

Compound	Influent (µg l <sup>-1</sup> )	Effluent (µg l <sup>-1</sup> )
Aldrin	500	<50
DDT	21000	<300
Endosulphan	18400	291
Endrin	3600	<100
2,4-dichlorophenol	180	<3.1

The presence of chlorine affects the selection of the materials for the construction of the reactor. Stainless steel may be inadequate for waste waters containing high levels of chlorine.

Claims by suppliers are that the system has advantages over thermal oxidation due to no NO<sub>x</sub> or SO<sub>x</sub> emissions, no dioxin production and no requirement for a stack or auxiliary fuels. Thus compared to thermal oxidation, WAO may be particularly amenable for dealing with waste waters containing sulphur, nitrogen and chlorine, which if incinerated are likely to give rise to acid gases.

A variant on wet air oxidation, LOPROX<sup>®</sup>, uses temperatures lower than 200 °C and pressures of 20 bar by utilising an iron based catalyst and an acidification stage at the front end of the technique. This technique may be particularly suitable for the pre-treatment of specific high COD containing effluent streams prior to biological treatment.

### 7.5.5 Super-critical water oxidation

Super critical water oxidation can be utilised for the removal of organic compounds from waste waters containing between 3 and 20% solids. It is particularly suited to the degradation of large organic molecules.

When water is heated to 374 °C and pressurised to 221 bar, it becomes supercritical and can facilitate the decomposition of organic chemicals. In the MODEC variant of the process, high-pressure pumps transfer the waste stream and oxygen through a pre-heater (which raises the temperature of the mixture to 300 °C) into a tubular reactor, where an exothermic reaction takes place at a temperature of about 600 °C. The products from the reactor pass through a cooler which forms part of the pre-heating circuit and are separated into a stream comprising

carbon dioxide and oxygen and a solids stream. The gas stream flows to a separator for return of excess oxygen to the process and recovery of liquid carbon dioxide.

Table 7.6 outlines destruction efficiencies for a number of compounds to which supercritical oxidation has been applied.

**Table 7.6 Destruction of hazardous compounds by supercritical oxidation**

Substance	Temperature (°C)	Reaction time (minutes)	Destruction efficiency (%)
1,2,4-trichlorobenzene	495	3.6	99.99
4,4-dichlorobiphenyl	500	4.4	99.9993
DDT	505	3.7	99.997
PCB 1234	510	3.7	99.99
PCB 1254	510	3.7	99.99
Dioxin	574	3.7	99.99995

Burgess (1998) also reports a range of destruction efficiencies. These are summarised in Table 7.7. Burgess reports that a SCWO plant in the USA with an influent TOC of greater than 50000 mg/l and amine bearing wastes up to a total of 5% of the total flow to effluent concentrations of 0-10 mg/l of TOC and 2.7 mg/l for ammonia. Nitrogen as nitrate was also reported as 6.4 mg/l. These results suggest removal efficiencies of 99.988% and 99.929% for TOC and organic nitrogen, respectively.

**Table 7.7 Destruction efficiencies for SCWO when applied to a range of waste waters/sludges**

Source	Temp (°C)	Contact time (mins)	Concentration (mg l <sup>-1</sup> )		Destruction efficiency (%)
			Influent	Effluent	
Industrial waste water	400	1	1840	27	98.5
	450	1	1840	15	99.2
	500	1	1840	4	99.7
Industrial sludge	400	30	30300	120	99.6
	450	10	30300	50	99.8
	500	5	30300	400	98.7
Mix of industrial waste water and sludge contaminated soil	400	4	39000	4520	88.4
	450	4	39000	831	97.9
	500	4	39000	429	98.9
	400	8	170	13	92.4
	450	4	170	9	94.6
	500	2	170	9	94.6

Any carbon present in the waste water is oxidised to carbon dioxide, which can be recovered as a liquid for sale. Halides, sulphur and phosphorus are oxidised to their respective mineral acids and are present in the effluent from the technique as mineral salts and insoluble metal oxides. These solids can be removed from the treated effluent and sent to landfill as a sludge.

Organic nitrogen present in the waste is converted to nitrogen gas which can be vented to atmosphere. Since oxidation is essentially complete, the technique does not require expensive plant to treat the exhaust gases.

The heat required by the technique is derived from the treated waste water and additional energy is not needed during normal operation. The main operating costs are associated with the use of oxygen.

### **Costs**

The cost for the treatment of waste by the MODEC SCWO process is estimated to be between £75 to £200/tonne of dry solids. This compares favourably with other techniques for the treatment of hazardous wastes. MODEC claim that the technique could prove attractive at medium-size waste water treatment works producing between 5 and 20 tonnes/day of dry solids.

### **7.5.6 Chemical Oxidation**

Chemical oxidation and the technology for its large-scale application are well established. Oxidation-reduction, or Redox, reactions are those in which the oxidation state of at least one of the reactants is raised while that of another is lowered.

Chemical oxidation is best utilised for dilute aqueous streams containing hazardous substances or for removing residual traces of contaminants after, for example, biological treatment. Chemical oxidation may be considered as a first treatment step if the target contaminant is not amenable to other treatment methods but removal efficiencies may be greatly reduced by suspended solids or other organics which will 'use up' the Redox potential provided by the chemicals. Operational costs may escalate and longer contact times may be required between the chemicals and the waste water. These two factors may result in a requirement for a larger reaction vessel with consequent capital cost implications.

The pH may need to be adjusted to maximise the Redox reactions and during the reaction heat may be liberated. Cooling systems must be considered, these again require space and energy.

The oxidation agents themselves may be a gas (e.g., chlorine), a liquid (e.g., hydrogen peroxide) or a solid (e.g., potassium permanganate).

### **7.6 Pre-treatment**

A number of waste water streams may require only relatively simple treatment prior to disposal, alternatively other waste streams may require conditioning prior to central treatment, for example in a biological plant. These streams can be given pre-treatment.

There are four main types of pre-treatment. These are:

- removal of water insoluble compounds;
- solids removal;
- pH adjustment;
- equalisation (balancing).

Each technique is discussed in more detail below.

### **7.6.1 Water insoluble compounds**

Water insoluble compounds, particularly oils, can be physically separated from a waste water stream by the use of separators. In general separators should be positioned as close as possible to the source of the insoluble compound(s) and should be the subject of regular checks. The separator should retain the insoluble compound or direct it to temporary storage. Whichever approach is adopted the recovered compounds should be regularly removed.

### **7.6.2 Solids removal**

Removal of solids from waste water can occur at several points in a treatment sequence. Grit removal by screening, filtration, or sedimentation is sometimes done as a preliminary step. The removal of sludge and other solids by means of clarification, filtration, or a special operation such as flotation can be carried out as a single solids removal step or in combination with the preliminary screening or a filtration step. The various techniques available for solids removal are discussed below.

#### **Sedimentation**

The settling rate of suspended solids out of the waste water is dependent on particle size and density. The smaller the particle size and the closer the density to that of water, the slower the settling rate. To improve settling rates coagulants and flocculant aids can be added to promote the formation of larger particles which will render them more settleable.

Clarifiers are usually large containment vessels that have a continuous waste water throughput. A conventional clarification system utilises a tank to rapidly mix chemicals with the waste water. The waste water is then subjected to slow agitation to promote particle growth followed by a quiescent settling tank. Provision for the removal of settled solids from the settling tank is also a necessary part of the system.

It is not unusual to see clarifiers used without the chemical addition step. They perform some solids settling as well as flow equalisation when used in this way.

#### **Flotation**

Flotation is an alternative to clarification and is utilised to remove suspended solids which have densities less than that of water. Flotation may also be applied to some systems with solids

slightly heavier than water. As with conventional clarifiers, coagulants and flocculant aids are frequently employed to produce large particles to enhance the efficiency of flotation.

Dissolved air flotation (DAF) is the most frequently used flotation process. It is particularly effective for the treatment of certain oily wastes following the addition of a flocculant.

## **Filtration**

The most common filtration system is the conventional gravity filter. It normally consists of a deep bed of granular media in an open-top tank. The direction of flow through the filter is downward and the flow rate is dependent solely on the hydrostatic pressure of the waste water above the filter bed. An alternative type of filter is the pressure filter. The basic approach is the same as for a gravity filter, except the tank is enclosed and pressurised.

Silica sand, anthracite coal, garnet, and similar granular inert materials are among the most commonly used filter media, with gravel serving as a support material. These filter media may be used separately or in various combinations. Multimedia filters may be arranged in relatively distinct layers. This is accomplished by selecting appropriate filter backwash flow rates, media grain size and media densities.

As waste water passes through the filter bed, the solids collect in the spaces between the filter particles. Periodically, the filter media must be cleaned to remove the accumulated solids. This is accomplished by backwashing the filter (reversing the flow through the filter bed). The flow rate for backwashing is adjusted in such a way that the bed is expanded by lifting the particles that make up the filter media a given amount. This expansion and subsequent motion provides a scouring action which effectively dislodges the entrapped solids from the media grain surfaces. The backwash is collected in a trough, fed to a storage tank, and recycled into the waste treatment stream. The backwash flow is continued until the filter is clean.

Filtration can be used as a sole treatment step or in combination with sedimentation or dissolved air flotation.

## **Evaporation**

Evaporation is a simple concentration process. Water is evaporated from a solution until the chemicals remaining in the waste water are concentrated to a level that allows their reuse in the process bath or the use of an alternative disposal route (e.g incineration). Although evaporation has large energy requirements, its simplicity and reliability are compensating factors.

## **Crystallisation**

This technique can be used on liquid waste streams containing potentially hazardous materials in the order 1-10% total dissolved solids. It would be predominantly used for the treatment of relatively low volume streams and typically as part of product recovery. It is inappropriate where waste waters are polluted with a number of contaminants.

### 7.6.3 pH control

pH control is frequently a necessary pre-treatment step for sedimentation, flotation and filtration to precipitate, for instance, heavy metals or to achieve the optimum pH for coagulation and flocculation. It is currently applied in many industrial effluent plants and has a wide applicability to waste streams of diverse physical and chemical composition.

pH control is a chemical reaction between an acid and a base which produces a specified pH range and may be used on liquids, slurries and sludges. Most frequently the target range is 6.5 to 7.5 i.e. a neutral solution. However, for subsequent treatment steps it may be desirable to have a different set point. Control may be carried out in batch or continuous flow and requires reaction tanks, agitators, monitoring and control capability, pumps and ancillary equipment for handling solids and/or liquids. Storage facilities will also be required.

The most common liquid acidic reagent used is HCl, although the use of CO<sub>2</sub> could also be considered. To achieve alkaline conditions NaOH or lime may be used. Lime is often used where continuous addition to a large flow is required. The lime may be added to a side tank which is continuously stirred and the suspension pumped into the waste water. The presence of CO<sub>2</sub> when using lime can cause scale formation in the receiving pipelines.

The treated stream should not change in physical form during pH control. This would lead to precipitation and solids build up in the reaction vessel. Gas evolution may also occur.

### 7.6.4 Equalisation (Balancing)

As described previously balancing may be used to ameliorate pH or temperature. It may also reduce peak loads on down stream techniques. Savings in the operational and capital costs of subsequent techniques may therefore off set the investment required for the balancing tanks and associated bunding.

Balancing tanks may require mixing to prevent settlement. If the effluent is of an organic nature, consideration must also be given for the period of time that waste waters can be held in the tanks without the occurrence of septicity.

## 7.7 Central Treatment Techniques

Central treatment is usually applied to waste water from a number of different sources and will in practice be the main treatment step for many processes.

The type of treatment applied will depend on the characteristics of the waste water. Figure 7.3 illustrates the approaches that can be adopted for predominantly organic and inorganic waste waters, respectively. The former are usually treated using biological treatment, the latter by chemical coagulation.

### 7.7.1 Biological Treatment

This option is usually considered where the waste water is predominantly organic and present in large volumes. Table 7.8 summarises some of the main biological treatment techniques together with their use.

**Table 7.8 Major biological treatment processes used for waste water treatment**

Type	Common name	Use*
<b>Aerobic processes:</b>		
Suspended-growth	Activated-sludge process	Carbonaceous BOD removal (nitrification)
	Conventional (plug-flow)	
	Complete-mix	
	Step aeration	
	Pure oxygen	
	Sequencing batch reactor	
	Contact stabilisation	
	Extended aeration	
	Oxidation ditch	
	Deep tank (90 ft)	
Deep shaft		
	Suspended-growth nitrification	Nitrification
	Aerated lagoons	Carbonaceous BOD removal (nitrification)
	Aerobic digestion	Stabilisation, carbonaceous BOD removal
	Conventional air	
	Pure oxygen	
Attached-growth	Trickling filters	Carbonaceous BOD removal, nitrification
	Low-rate	
	High-rate	
	Roughing filters	Carbonaceous BOD removal
	Rotating biological contactors	Carbonaceous BOD removal (nitrification)
	Packed-bed reactors	Carbonaceous BOD removal (nitrification)
Combined suspended- and attached-growth processes	Activated biofilter process, trickling-filter solids-contact process, biofilter activated sludge process, series trickling-filter activated-sludge process	Carbonaceous BOD removal (nitrification)
<b>Anoxic processes:</b>		
Suspended-growth	Suspended-growth denitrification	Denitrification
Attached-growth	Fixed-film denitrification	Denitrification

Type	Common name	Use*
<b>Anaerobic processes:</b>		
Suspended-growth	Anaerobic digestion	
	Standard rate, single-stage	Stabilisation, carbonaceous BOD removal
	High-rate, single-stage	Stabilisation, carbonaceous BOD removal
	Two-stage	Stabilisation, carbonaceous BOD removal
	Anaerobic contact process	Carbonaceous BOD removal
	Upflow anaerobic sludge-blanket	Carbonaceous BOD removal
Attached-growth	Anaerobic filter process	Carbonaceous BOD removal, waste stabilisation (denitrification)
	Expanded bed	Carbonaceous BOD removal, waste stabilisation
<b>Combined aerobic, anoxic, and anaerobic processes:</b>		
Suspended-growth	Single- or multi-stage processes, Various proprietary processes	Carbonaceous BOD removal, nitrification, denitrification, phosphorus removal
Combined suspended- and attached-growth	Single- or multi-stage processes	Carbonaceous BOD removal, nitrification, denitrification, and phosphorus removal
<b>Pond processes:</b>		
	Aerobic ponds	Carbonaceous BOD removal
	Maturation (tertiary ponds)	Carbonaceous BOD removal (nitrification)
	Facultative ponds	Carbonaceous BOD removal
	Anaerobic-ponds	Carbonaceous BOD removal (waste stabilisation)

\* Major uses are presented first; other uses are identified in parentheses

Of the treatment options being considered, biological treatment is perhaps the most difficult to demonstrate the effectiveness of. The biological system often comprises a consortia of micro-organisms which may be adversely affected by one or more components of the waste water. Though it may be possible to identify sites where the technique has been used for a similar purpose, small differences between the composition of the waste waters can have a dramatic impact on the viability of biological processes.



<b>AV 5.5/AV 1.5</b>	<b>Spray tower scrubbers</b>
<b>Pollutants</b>	VOCs, odours and particulates
<b>Description</b>	A tower in which the waste gas flow upwards or horizontally through a countercurrent, cross-current or co-current of scrubber liquid produced as at a series of nozzles.
<b>Availability</b>	High
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• efficiencies depend upon droplet size, gas velocity, liquid:gas ratio, and droplet trajectory. Efficiency improves with spray nozzle pressure (&gt;1400 to 2800 kPa), and liquid:gas ratios (4-13 l/m<sup>3</sup>). Spray droplets are typically 0.1-1 mm diameter;</li> <li>• less effective in removing VOCs than other forms of absorption systems - generally restricted to removal of high solubility gases such as SO<sub>2</sub> and NH<sub>3</sub>;</li> <li>• multi-stage systems often employed to improve mass-transfer;</li> <li>• pressure drop across a tower is usually 0.25-0.5 kPa, and a typical liquid:gas ration is in the range 4-13 litres water/m<sup>3</sup> gas;</li> <li>• droplet diameter and distribution are critical design parameters - typically, droplets of diameter 200-400 µm needed for VOC removal;</li> <li>• spray nozzle plugging can be problematic.</li> </ul>
<b>Environmental impacts</b>	Disposal of scrubbing liquid
<b>Costs</b>	

Feature		Comments
<b>GROWTH RATE INHIBITION</b>		
Quick results	√	Within 1 day, but requires inoculation from preculture established 16h before start of test.
Fastest/simplest method for application	√	
No expensive/specialised equipment required	×	Optical light spectrophotometer needed for making absorbance measurements.
Accommodates several effluents concurrently	√	But capacity limited; 3-4 samples per day per operator is a realistic clearance rate.
<b>INHIBITION OF ANAEROBIC SLUDGE DIGESTION</b>		
Quick results	√/×	48 hour incubation
Fastest/simplest method for application	√	
No expensive/specialised equipment required	√	
Accommodates several effluents	√	Serum bottle technique allows large concurrently number of treatments to be placed in an incubator.
<b>MICROTOX</b>		
Output		Appeal of this technique lies in the speed with which it gives results, but their significance in isolation is dubious; requires calibration against response in other tests.
Quick results	√√	Within 1 hour.
Fastest/simplest method for application	√	
No expensive/specialised equipment required	×	Requires proprietary luminometer and reagents which can be expensive
Accommodates several effluents concurrently	√	

**Table 7.10 Characteristics of screening methods suggested for assessing treatability**

Feature		Comments
<b>ZAHN-WELLENS DIE-AWAY</b>		
Quick results	×	Depends on sample, but incubations of 1 week would be typical.
Fastest/simplest method for application	√	
No expensive/specialised equipment required	√/×	Facilities required to perform analyses: COD a minimum requirement.
Accommodates several effluents concurrently	√	Limited only by the sample-handling rate at the analysis step(s).
<b>RESPIROMETRY</b>		
Output		Greater capital investment required, but by generating continuous data, has the advantage of filling in the gaps in information that occur during the sampling intervals of other methods.
Quick results	×	Depends on sample, but incubations of 1 week would be typical.
Fastest/simplest method for application	√/×	Modern automated instruments with PC control allow tests to run without operator attendance; performance is also instantly visible on screen.
No expensive/specialised equipment required	××	Automated devices cost in the range £k25-50.
Accommodates several effluents	√	But limited by the number of recording concurrently channels available, typically 8 or 12.

Carbonaceous BOD, the biological oxygen demand (BOD) of organic compounds in the waste water, is the main issue for this sector and will generally be more important than the other form of BOD which is associated with nitrogen containing compounds.

The main biological techniques of relevance to this sector, in order of importance are:

- aerobic;
- anaerobic.

The performance of both of these techniques can be enhanced by the utilisation of:

- fixed film processes;
- bioaugmentation;
- adsorption.

Each of these techniques is discussed below, together with the potential use of constructed wetlands (reed beds).

## **Aerobic techniques**

There are many variants of this process, some of which are listed in Table 7.8, and for each variant there are many different designs. As an overview it can be said that the activated sludge process is used extensively in the sector, and is probably the most cost effective method of removing biodegradable organic compounds present in aqueous waste streams.

An activated sludge system should be preceded by pH control to approximately neutral, equalisation of the waste stream and suspended solids removal. It is a safe and reliable technique and for carbonaceous BOD removal is relatively uncomplicated and inexpensive to operate. Nitrification and phosphorous removal is possible but the complexity of operation may require a special design.

Activated sludge treatment involves an aeration step, followed by solid-liquid separation, with recycle of a portion of the solids (the activated sludge). The basic system has an open tank for the mixing of the biomass with the waste water and air, followed by a clarifier. The aeration step encourages the growth of bacteria that perform the hydrolysis and oxidation reactions. The system is energy intensive with 10% of the operational costs based on the energy required to provide the aeration.

The traditional activated sludge plant requires a relatively large area. In some industrial applications this may limit its application hence some variants have been designed to overcome this problem. The deep tank activated sludge process is now widely applied. In addition, to space savings it also has the advantage of being enclosed, thus allowing the collection of odorous and volatile compounds, and making more efficient use of the available oxygen, which improves removal efficiencies. Deep tank techniques will, however, generally cost more to construct than conventional aerobic systems.

There are a number of important factors that need to be considered when utilising aerobic biological techniques in this sector. These include:

- **volatile emissions** - If volatile organics are present in the effluent, these may be stripped from the effluent by the introduction of the air. The need to collect the gases for treatment to avoid cross media contamination should be assessed. If VOC emissions are judged to be significant tanks may have to be covered and the gases collected;
- **inhibition** - The biological system relies on the establishment of an active mass of bacteria with the enzymes able to break down the contaminants. However some chemicals can inhibit the growth or respiration of the biomass. Consequently reduced efficiency in treatment is possible as is the complete failure to treat the waste water. More subtle effects may be that the settlement characteristics of the biomass is affected and solids appear in the treated effluent. The possibility or extent of inhibition for any given waste water is usually only predictable using inhibition tests. Such

methods for assessing the treatability of industrial waste waters are published by HMSO (1983, 1989);

- **acclimatisation** - The biomass is a living and often changing entity. Consequently given a slow increase in the concentration of a contaminant in the waste water the biomass may be able to adapt and begin to treat the contaminant. Shock high concentrations may, however, still prove fatal. Thus equalisation and the removal of peak concentrations may have to be considered;
- **solids** - The activated sludge technique generates waste sludge. If contaminated with metals, pathogens, pesticides, high concentrations of ammonia or chlorinated chemicals the disposal options may be limited to landfill or incineration. The disposal strategy for the sludge must be considered for its potential for cross-media contamination;
- **recalcitrant organics** - These are organic chemicals that are resistant to biological treatment and which when released untreated into the receiving water may cause adverse impacts on the ecosystem or aesthetic effects. They may also over time, biodegrade and the subsequent products may represent a biological oxygen demand on the receiving water. Furthermore if the effluent is discharged to sewer these chemicals are likely to pass through the sewage treatment works to the aquatic environment;
- **toxicity** - Chemicals such as herbicides may not be toxic to the biomass but if they are recalcitrant and survive the treatment process they may adversely affect organisms in the receiving water;
- **odour** - May be due to the volatilisation of chemicals in the waste water or degradation by-products. However septicity of sludges and poor sludge management procedures can also generate odour;
- **nutrients** - In cases where waste waters contain large amounts of organic matter from relatively pure sources, the waste water may not contain the correct balance of carbon, nitrogen, oxygen, hydrogen phosphorous and sulphur. Limitation of growth may therefore occur rendering the biological process less efficient. The BOD/N/P ratio of 100/5/1 by weight is used as a guideline demonstrating suitability for biological treatment. However, the ratios are based on a yield of 0.5 g cell biomass per g BOD removed, and a sludge composition of 10% N and a 2% P on a dry weight basis. A variant of the ASP is extended aeration and has been seen to be effective at a nutrient ratio of 100/0.8/0.2. The addition of nutrients or co-treatment with sewage may also be considered as a method of providing the required nutrient balance.

A process operator may be expected to demonstrate that these issues have been considered prior to the installation of a new aerobic technique. It may also be of benefit for existing users to consider whether their technique needs modification to address these issues.

## **Anaerobic techniques**

Anaerobic digestion is a biological treatment process for the degradation of simple organics in an air-free environment. Part of the carbon substrate is used for cell growth and the rest is converted to methane and carbon dioxide. The microbiology is complex and requires a consortia of organisms to achieve methanogenesis. Conditions such as pH and loading must be closely controlled. Organics such as chloroform have a very inhibitory effect on the technique.

The technique is favoured for very strong BOD streams and has been widely used in the brewing industry. It may therefore have an application in the treatment of fermentation spent liquors but care should be taken if the product of the fermentation process has antimicrobial properties. In general anaerobic techniques will be of far less importance than aerobic ones for this sector.

## **Improving the performance of biological techniques**

A number of techniques are available for improving the performance of biological techniques. The main ones are:

- fixed film techniques;
- bioaugmentation;
- biological treatment with adsorption.

Each of these techniques are summarised below.

### **(a) Fixed Film processes**

The micro-organisms that form the biological community grow as biofilms on a support medium. If they are inhibited they will remain in the system although inactive. In the normal suspended growth system, organisms that are not reproducing are washed out of the reactor. Consequently a fixed film system is believed to be more tolerant to fluctuations in waste water composition and more able to stand toxic shocks.

However, it is not uncommon for the biofilm to grow and become detached from the support media. This process is known as sloughing and can lead to high concentrations of suspended solids in the final effluent.

### **(b) Bioaugmentation**

Bioaugmentation involves the addition of material to deal with compounds that are resistant to normal biological treatment. There are two main variations; supplementary bacteria and immobilised enzymes, respectively.

If the performance of an existing effluent treatment plant needs to be updated, a programme of bioaugmentation involves little or no capital cost but entails a higher operating cost owing to the continued use of supplementary bacteria or enzymes. If a new effluent treatment plant needs to be built then bioaugmentation will result in both increased capital and operating costs.

The general efficacy of bioaugmentation has yet to be proven conclusively. Only by conducting laboratory or pilot tests may its use be demonstrated for a particular application and estimates made of its cost implications.

#### *Supplementary bacteria*

Supplementary bacteria may be used for the treatment of organic compounds such as pentachlorophenol which are resistant to normal biological treatment. The main forms of supplementary bacteria are Dried Bacteria Culture (DBC) and Liquid Bacteria Culture (LBC). Both cultures contain nutrients and pH buffers to enable the bacteria to rapidly metabolise organic compounds. DBC must be added to warm water (30 to 40 °C) and left for a suitable period (e.g. 1 to 4 hours) prior to use.

Laboratory studies are conducted to identify the main components of the waste water that are resistant to normal treatment and to isolate microbes capable of treating them. The isolates are combined to produce an inoculum which can then be used to treat the waste water.

The bacteria culture is dosed into the biological treatment process. A relatively high dose is required initially but this is then reduced until only a maintenance dose is needed.

#### *Immobilised enzymes*

Enzymes act as catalysts for biochemical reactions, increasing reaction rates and facilitating the break down of large organic molecules into smaller molecules which are more easily biodegraded by bacteria. Since enzymes added in solution would be rapidly washed out of a reactor, a range of physical and chemical methods have been developed to fix or immobilise enzymes so that they can be constantly reused. Methods include immobilising enzymes in either pellets or beads which can be used in packed bed reactors, or in fibres or membrane structures for use in suspended-growth biological treatment plants.

#### **(c) Biological treatment with adsorption**

The technique involves biological treatment in a suspended growth system with dosing of powdered activated carbon (PAC) to the reactor/aeration tanks. Biological treatment is usually a single or two stage activated sludge technique but can include an anaerobic pre-treatment stage. The technique can be used in either batch or continuous mode. This system will only be beneficial if the target substances adsorb to the PAC. Therefore, small scale tests should be performed to confirm that adsorption is occurring.

The PAC protects the biological system from toxic shock upset, greatly increasing the robustness, stability and performance of both carbonaceous oxidation and nitrification (ammonia removal). Long sludge ages >20 days (sludge residence times) are achievable increasing removal rates for slowly degradable recalcitrant organics. Emissions of volatile organic compounds from the aeration basin are greatly reduced due to adsorption onto the carbon. Nitrification inhibition is also reported to be reduced. The technique is generally applicable in the COD range 50 mg l<sup>-1</sup> - approximately 100 000 mg l<sup>-1</sup>.

Granular activated carbon (GAC) columns can be used as an alternative to PAC dosing. However, PAC is cleaned in the biological system and so overall usage of carbon compared to GAC columns is much lower. In addition, PAC is cheaper than GAC.

Table 7.11 provides a comparison of the performance an activated sludge process on its own with one coupled with PAC, albeit for a waste water arising from a different sector. It suggests that whilst PAC may improve performance for some pollutants (COD), for others performance may actually deteriorate.

**Table 7.11 Comparison of performance of ASP vs PACT® for the treatment of shale oil retort water**

Parameter or Compound	Influent mg l <sup>-1</sup>	ASP Effluent mg l <sup>-1</sup>	PACT® Effluent mg l <sup>-1</sup>
COD	23 700	8510	2510
BOD	6220	27	650
Phenols	71.4	0.2	2.88
Cyanide	60.1	0.65	39.3
Thiocyanate	191	16.2	229

### Constructed wetlands

Constructed wetlands may be used for waste water treatment but their efficiency and ability to remove the pollutant load should be carefully assessed prior to installation. Man-made or constructed wetlands have been designed to improve the efficiency of natural biological processes. In most cases they use plastic liners to improve containment. It is envisaged that artificial wetlands would be considered where:

- space is available to build the wetland;
- the waste water contains predominantly organic/biodegradable wastes and is of a relatively low strength (<2000 mg BOD<sub>5</sub> l<sup>-1</sup>);
- polishing of a treated effluent is required.

The advantages of using wetlands are:

- low operational costs and skill base;
- facilitating regeneration of the area's natural habitats;
- providing an environmentally friendly image for the company; and
- relatively low capital costs.

It is important to ensure that there is sufficient land available for the wetland and that it is neither hydraulically or organically, under or over loaded. Gravel rather than soil filled beds allow a faster flow of waste water through the bed by creating a more open structure.

Traditionally the flow of the waste water has been horizontally through the media of the reed bed. Vertical flow (VF) reed beds are stratified with layers of gravel and, on the surface, sand. The waste water is applied to the surface and flows through the layers of media. The flow is



intermittent and forces air through the bed. VF beds improve treatment and reduce the land needed for treatment but they are more complex in their design and operation.

The correct sizing of the reed bed is essential. The key parameter being the treatability of the waste water. The ICI plant at Billingham is probably the best known application in the UK and pilot plant studies were performed to ensure that the waste was treatable by this method.

The site at ICI Billingham is approximately 3600 m<sup>2</sup> treating 3000 m<sup>3</sup> day<sup>-1</sup> of settled waste water, the COD is in the range of 740 to 3500 mg l<sup>-1</sup>, and BOD/day of 3.5 tonnes. The treatment efficiency is claimed to be 95% BOD removal. The design comprises vertical and horizontal flow units.

The key cost elements are the liner and the delivery price of the gravel. If soil is used the area required will be dramatically increased and may render the project impracticable.

### **Advances in biological treatment**

The pressures to improve biological treatment are likely to relate to energy efficiency, size and the need to meet more stringent consents containing nitrogen and phosphorous limits. Response to these drivers will be:

- application of techniques designed and operated for nutrient removal. These units will be more complex and may, for the chemical sector, require a higher degree of on-line monitoring and control;
- combined treatment techniques are being developed to deal with size constraints. These techniques include activated sludge plants with filter membranes within the bioreactor. They retain a higher suspended solids concentration and are smaller. They have recently been introduced in Japan for domestic applications.

### **7.7.2 Chemical Coagulation**

The technique is used primarily for the removal of suspended solids, although it will also remove some dissolved organic compounds and micro-organisms. The most commonly used chemical coagulants are listed in Table 7.12.

**Table 7.12 Commonly used chemical coagulants**

Chemical	Form supplied
Aluminium sulphate (alum)	Liquid at 8% as $Al_2O_3$ or solid
Ferric sulphate	Liquid at 40% as $Fe_2(SO_4)_3$
Ferric chloride	Crystalline or liquid
Poly Aluminium Chloride	Liquid at 10% as $Al_2O_3$
Poly Aluminium Sulphate	Liquid as 8.3% as $Al_2O_3$
Cationic polymers	Solution or full strength dry
Anionic polymers	Full strength dry
Non-ionic polymer	Full strength dry

This technique involves the addition of a dissolved chemical to the waste water with rapid dispersion and mixing. The pH of the dosed water is adjusted (if necessary) to a level at which the dissolved chemical precipitates, usually in the form of a hydrated hydroxide. This pH adjustment is typically by the addition of acid or lime. In some instances a further flocculant aid chemical is added to improve solid/liquid separation.

The coagulated and flocculated particles (floc) attract and adsorb other dissolved and suspended matter. The floc can then be separated from the water by settlement or flotation. The settling of the coagulated particles and decantation of supernatant can be achieved by:

- flotation - The use of small air bubbles to float the coagulated particles to the surface of the water, from where a scraper removes them;
- rapid deep bed filtration - The direct or post sedimentation/flotation application of the water to a filter, normally consisting of graded gravel and sand.

The use of chemical coagulants produces a sludge of the coagulated chemical and the organics and other substances which have adsorbed onto the particles. This sludge can be thickened and dewatered to reduce its volume. The technique re-partitions the target pollutant from the waste water to the sludge and the disposal of the sludge therefore becomes the main operational constraint on its use.

The technique for establishing the best coagulation regime is known as jar testing. The contaminated water is treated with a number of coagulants at a range of doses and pH. A standard stirring regime and settlement time is applied to each of the samples and the residual contaminant measured. This procedure will enable the optimum dose and conditions to be established. Table 7.13 shows the performance of some chemical coagulants.

**Table 7.13 Removal performance by chemical coagulants**

Substance	Coagulant	Upper pH	Lower pH	Removal (%)	Feed conc (mg l <sup>-1</sup> )
Inorganic mercury	Al		>8	70	
	Fe		>8		
Cadmium and compounds	Fe			98	0.5
DDT	Fe	12		100	
HCB	Fe	12		59	
Aldrin	Fe	12	6	100	
Dieldrin	Fe			50	
Endrin	Fe			43	
Polychlorinated Biphenyls				30-40	
tributyltin compounds				>90	
trichloroethylene	Fe	12		36	
perchloroethylene	Fe	12	6	30	

**Process costs**

The following costs are derived from WRC 1977 and Booker 1988, and updated to Q3 97.

**(a) Capital costs**

Assuming that the capital costs consist of a chemical dosing plant and a simple sedimentation tank:

$$\text{SED TANK } \text{£'000} = 93.9 \times \left( \frac{\text{FLOW}}{\text{URATE}} \right)^{0.96}$$

$$\text{CHEM PLANT (£'000)} = 83.6 \times (\text{FLOW})^{0.46}$$

URATE: upflow rate in sedimentation tank (m/hr) typically 2 to 4

**(b) Operating costs**

$$\text{LIMECOST (£/year)} = \text{FLOW} \times 0.365 \times \text{DOSE} \times \text{COST}$$

- COST: lime cost (£/tonne)
- FLOW: plant throughput (Ml d<sup>-1</sup>)
- DOSE: lime dose (mg l<sup>-1</sup>) of plant throughput
- Lime costs: approx. £65/tonne.
- Typical dose: 150-200 mg l<sup>-1</sup> for softening of very hard water.

## 7.8 Polishing Treatment

Polishing is applied as a final treatment stage and is usually used to remove the constituents of waste water that have proved resistant to earlier treatment. In certain circumstances some polishing techniques may be applied as special treatment techniques, although this will be comparatively rare. It is usually preferable to apply polishing techniques when the bulk of the polluting load of the waste water has been removed and it can be focused on the small proportion of problem compounds that remain.

The polishing techniques addressed in this section are:

- ozone;
- activated carbon;
- zeolites;
- membranes;
- ion exchange.

There are a number of variations on these techniques and these are also discussed.

### 7.8.1 Ozone (O<sub>3</sub>) based systems

A wide range of ozone based techniques are available. They are particularly useful for dealing with recalcitrant COD. The main techniques are:

- ozone on its own;
- ozone with ultra-violet radiation;
- ozone with ultra-violet radiation and hydrogen peroxide;
- ozone with adsorption.

All four techniques have in common the generation of ozone. This is usually achieved by discharging a high voltage electrical current through dry air or pure oxygen. Dry air must be used or else nitric acid is formed and efficient cooling of the ozone production elements is required. Recent developments in ozone generation use medium rather than high frequency electric currents, and oxygen rather than air. This reduces energy consumption and increases the ozone concentration substantially. These developments should make the technique more economic.

The presence of high concentrations of oxygen increases the fire hazard. The instigation of proper safety procedures and the minimisation of possible ignition sources are essential. The partial pressure of oxygen above effluents saturated with oxygen is about five times that in air therefore oxygen will tend to desorb from the treated effluent into air. In the event of a large discharge into still receiving waters with little wind the oxygen enriched air could accumulate causing a flammability hazard. Outfalls should therefore rapidly mix the treated effluent with receiving waters. Off gases generated contain ozone and may also contain NO<sub>2</sub> and VOCs. Treatment of these gases may be required.

### (a) Ozone on its own

Ozone on its own can be used for the removal of recalcitrant COD or to convert it to biodegradable COD. It can also be used for the removal of colour and odour as well as disinfection. Phenols and alkyl phenol ethoxylates can be selectively destroyed by ozone alone. This technique is now well established and many examples exist of its successful application in the chemical industry. Table 7.14 shows some removal efficiencies that can be achieved by ozone for the treatment of a number of organic compounds.

**Table 7.14 Removal efficiencies of substances for which ozonation is a potential treatment process**

	Dose (mg l <sup>-1</sup> )	Contact (mins)	% Removal	Feed conc. (µg l <sup>-1</sup> )
Aldrin	240		100	
Dieldrin	36		50	10
Dichlorvos *	3 to 5		96 to 100	70
	>20		high	10 000
1,2-dichloroethane	20 (pH9 to 10)		80	
trichlorobenzene	6		63	
	20		74	
atrazine	3		42	0.74
	91 mg l <sup>-1</sup>	100	100	20 300
simazine	3		53	0.25
fenitrothion	>35 mg l <sup>-1</sup>		high	
azinphos-methyl *	3 to 5		96 to 100	70
malathion	3 to 5		55 to 88	100
	26		100	
trichloroethylene	20		99	
perchloroethylene	20		72	

\* Using generic data for organo-phosphorous pesticides

### (b) Ozone with ultraviolet irradiation

This technique uses reactors fitted with ultra-violet (UV) lights and run under pressure to keep the ozone in solution. Hydroxyl radicals are generated by UV reacting with the ozone to form oxygen singlets which themselves react with water. The reaction of UV, ozone and chlorinated hydrocarbons produces water and hydrochloric acid. The use of combined UV/ozone systems instead of ozone alone allows a wider range of organic substrates to be treated in a shorter reaction time. The wavelength of the UV source may be modified to break selected chemical bonds.

The use of this technique may be limited by turbidity. High turbidity results in poor transmission of UV light through the waste water and hence limits removal efficiencies.

### **(c) Ozone with ultra violet irradiation and hydrogen peroxide**

Hydrogen peroxide is used in this technique to enhance oxidation by generating more hydroxyl radicals. The system may be especially useful for the oxidation of aromatic halides which are good adsorbers of UV light. The hydroxyl radical is produced at equimolar concentrations of ozone and hydrogen peroxide. At high concentrations of hydrogen peroxide it acts as a scavenger for the hydroxyl radicals.

This system appears to give the highest oxidation rates with lowest ozone usage, although its use has yet to be widely demonstrated. It should be noted that ammonia competes with the target organic pollutants in the waste water for the hydroxyl radicals and thus the technique is best applied to effluents that are well-nitrified or have low ammonia concentrations.

### **(d) Ozone with adsorption pre-concentration**

This is a recently developed technique and utilises oxygen rather than air for the generation of the ozone. It is intended to be used to deal with specific high toxicity compounds that may be present in relatively low concentrations in effluents with a high COD loading.

The waste water is mixed with an appropriate metal (non toxic) hydroxide compound. The target substances are adsorbed onto the hydroxide and removed from the waste water. This forms a slurry which is then mixed with ozone and the target substances destroyed in a reaction catalysed by the metal hydroxide.

Using this method, an effluent from a carpet manufacturer required an ozone dosage of  $68 \text{ mg l}^{-1}$  to destroy, dieldrin, permethrin and also cyfluthrin, propetamphos and diazinon to less than a total of  $8 \text{ } \mu\text{g l}^{-1}$ . However, when the oxidation process was applied directly to the effluent (without prior adsorption), an ozone dosage of  $1200 \text{ mg l}^{-1}$  combined with  $\text{H}_2\text{O}_2$  at  $600 \text{ mg l}^{-1}$  and UV at  $1.12 \text{ kW h l}^{-1}$  did not destroy those substances significantly. This is because the COD was in excess of  $1000 \text{ mg l}^{-1}$  compared to the target substances which were in the  $100 \text{ } \mu\text{g l}^{-1}$  range.

This case study demonstrates that the technique relies on the adsorption step to concentrate the target substances. If the substances are not adsorbed they will not be treated effectively. Consequently the adsorbent and conditions (e.g pH) used are essential and should be reviewed on a case by case basis.

### **(e) Comparative performance of ozone based techniques**

Comparisons have been made of the treatment of dichloromethane using various combinations of UV irradiation, ozone and hydrogen peroxide addition (see Table 7.15). The test conditions were not given but comparability is assumed. The results indicate the importance of contact time for the oxidation process and show that the best treatment performance is achieved using the combined systems.

**Table 7.15 Comparison of combination of UV irradiation, ozonation and hydrogen peroxide treatment for the oxidation of dichloromethane**

Dichloromethane: Initial Concentration 100 mg l <sup>-1</sup>	Reaction Time	
	15 mins	25 mins
UV	59 mg l <sup>-1</sup>	42 mg l <sup>-1</sup>
UV + hydrogen peroxide	46 mg l <sup>-1</sup>	17 mg l <sup>-1</sup>
ozone + hydrogen peroxide	32 mg l <sup>-1</sup>	21 mg l <sup>-1</sup>
UV + ozone	36 mg l <sup>-1</sup>	16 mg l <sup>-1</sup>
UV + ozone + hydrogen peroxide	19 mg l <sup>-1</sup>	7.6 mg l <sup>-1</sup>

### Costs

Both the capital and operating costs of ozone treatment are high. The high capital cost is mainly due to the large expense of ozone generation equipment, and the high operating costs are mainly due to significant electrical usage.

These costs are themselves very dependent on the amount of ozone used to achieve the required removal of the substances. Only by conducting laboratory or pilot plant studies can an accurate estimate of the costs be established for a particular process.

Costs updated for Q3 1997 from Booker 1988.

#### Capital costs

OZONE GENERATOR (£'000)	$108.4 + 7.9 \times (\text{ODOSE} \times \text{FLOW})^{0.8}$
BUILDING (£'000)	$2.0 \times (\text{ODOSE} \times \text{FLOW})^{0.64}$
CONTACT TANK (£'000)	$7.3 \times (\text{FLOW} \times \text{CTIME})^{0.48}$

ODOSE	applied ozone dose (mg/l)
CTIME	contact time (minutes)
FLOW	MI/day

#### Operating Costs

These costs are for the traditional generation of ozone.

$$(\text{£'000/year}) = 0.365 \times \text{ODOSE} \times \text{FLOW} \times (0.25 \times \text{ECOST} + 0.02 \times \text{WCOST})$$

ECOST	electricity cost (p/kWh)
WCOST	cooling water cost (p/m <sup>3</sup> )

### 7.8.2 Activated carbon adsorption

Adsorption is defined as the adhesion of dissolved molecules to the surface of solid bodies with which they are in contact. Activated carbon has two properties that makes it an effective and economical adsorbent. These are:

- a high surface area per unit volume which results in a large number of potential adsorbent points; and
- a high hardness value, which promotes reuse and longer lifetimes.

Activated carbon comes in two main forms:

- granular activated carbon (GAC);
- powdered activated carbon (PAC).

Each of these are discussed in more detail below.

#### Granular activated carbon (GAC)

The adsorption process typically is preceded by preliminary filtration or clarification to remove insolubles. The waste water is then contacted with granular activated carbon (GAC) so that adsorption can take place. Each activated carbon bed has a finite number of adsorption points and ultimately these become saturated and the target compounds are no longer removed from the waste water. In general GAC can deal with relatively wide variations in flow and concentration.

Normally, two or more beds are used so that adsorption can continue while a depleted bed is reactivated. Reactivation is accomplished by heating the carbon to between 870 °C and 980 °C to volatilise and oxidise the adsorbed contaminants. Oxygen in the furnaces is normally controlled at less than one percent to avoid excessive loss of carbon by combustion.

At each regeneration, a proportion of the GAC will be lost, typically about 10%. This would be replaced by fresh GAC. There is therefore a gradual 'turnover' of the carbon in the bed. This continuous renewal should be adequate to maintain the overall quality of the GAC in the bed.

Regeneration of GAC would normally be carried out by specialist companies, operating regeneration furnaces. These companies will transport GAC to and from the regeneration site. As regeneration is relatively expensive, GAC beds are usually sized to give a period of at least six months between regenerations.

GAC capacity for a specific substance can be reduced by the presence of other organics, which compete for adsorption sites and interfere with the kinetics of adsorption. The treatment of coloured waters may suffer from this phenomenon.

The capacity of various GACs for a specific substance in a waste water can be estimated from batch laboratory tests. The adsorption rate is then determined from rapid column tests and computer modelling. The data obtained from these sources are used to design the plant and specify the best GAC for the application.



Carbon adsorption is particularly applicable in situations where organic material is present in the waste water in low concentrations that are not generally amenable to treatment by other techniques. It is commonly applied as the final polishing step for the removal of non-biodegradable substances, often after a biological treatment stage.

### Powdered activated carbon (PAC)

Powdered activated carbon (PAC) is dosed to and mixed with the waste water as a slurry. The PAC is removed from the waste water by a subsequent treatment technique, such as sedimentation or filtration. It is commonly added to the waste water at the same point as inorganic coagulants.

PAC is superior to GAC in terms of its specific capacity for adsorbing organic compounds but it is usually used on a once only basis, being disposed of with the sludge from the sedimentation tank. Occasionally the PAC can be regenerated when the quantity used justifies it but not in as cost-effective a manner as GAC.

PAC can be used to adsorb organic compounds (and others). The adsorptive capacity varies depending on the activated carbon type and on the organic chemical being adsorbed. PAC is usually preferred to GAC where the demand for adsorptive removal of organics is intermittent or variable, as the PAC can be dosed as and when necessary.

### Costs of PAC

The cost estimates here are derived from WRc 1977, Booker 1988 and Walker 1991 and updated for Q3 1997.

#### (a) Capital costs

$$\text{PAC dosing (£'000)} = 2.8 \times (\text{FLOW} \times \text{PDOSE})^{0.41}$$

PDOSE                      PAC dose (mg/l)

#### (b) Operating costs

PAC DOSING

$$(\text{£'000/year}) = 3.65 \times \frac{\text{PDOSE} \times \text{PPER} \times \text{FLOW}}{12} \times \left( \frac{\text{PCOST}}{10000} + \frac{\text{DISP}}{100 \times \text{TSOL}} \right)$$

PPER	period that PAC is applied (months)
PCOST	cost of virgin PAC (£/tonne): Typical PCOST = £500
DISP	sludge disposal cost (£/tonne)
TSOL	total solids (tonnes)
FLOW	MI day <sup>-1</sup>

## Costs of GAC adsorption

The costs are derived from WRc 1977, Booker 1988 and Walker 1991 and updated to Q3, 1997.

Calculations or pre-design experiments will determine the volume of carbon required and its life. The calculations of costs are based on the Empty Bed Contact Time (EBCT) required for satisfactory reduction in contaminant levels and the flowrate of water to be treated. The capital costs are for the construction of plant and the initial purchase of GAC. The operating costs are related to the regeneration requirements, its cost and frequency.

### (a) Capital costs

GVOL	$0.694 \times \text{FLOW} \times \text{EBCT}$
GAC PLANT (£'000)	$20.4 \times (\text{GVOL})^{0.64}$
GAC COST (£'000)	$\text{ROW} \times \text{CCOST} \times \text{GVOL} \times 10^{-6}$
GVOL	GAC volume required
EBCT	empty bed contact time (mins)
ROW	GAC bed density ( $\text{kg}/\text{m}^3$ )
CCOST	cost of virgin GAC (£/tonne)
FLOW	plant throughput ( $\text{Ml}/\text{day}$ )

### Example

A flowrate of  $500 \text{ m}^3/\text{day}$ , requiring an EBCT of 15 minutes in GAC costing £1500/tonne and of density  $450 \text{ kg}/\text{m}^3$

Plant cost	£58,600
GAC cost	£3,500.

### (b) Operating costs

These are for regeneration.

$$(\text{£'000}/\text{year}) \quad \frac{12 \times \text{GVOL} \times \text{ROW} \times (\text{RCOST} + \frac{\text{LRGEN} \times \text{CCOST}}{100})}{100}$$

REGT	period between regeneration (months)
LRGEN	loss of GAC on regeneration (%)
RCOST	regeneration cost (£/tonne)

### Example

It is assumed that a period of two months is required between regenerations, that 10% of the GAC is lost during each one and the cost of one regeneration is £800/tonne.

Operating cost = £8900/year

Note: This example does not include labour and maintenance of the plant.

Table 7.16 shows comparative costs for the use of GAC and PAC, albeit in a different sector from the one considered in this study.

**Table 7.16 Example costs comparing PACT<sup>®</sup> with GAC absorption for landfill leachate treatment at Stringfellow Quarry California**

Costs	PACT <sup>®</sup>	GAC
Capital Costs	£1 130 000	£800 000
Annual Operating Costs		
Chemicals	£53 300	£50 000
PAC	£46 600	
GAC		£1 200 000
Power	£43 300	£20 000
O&M	£146 600	£100 000
Total	£289 800	£217 000
Annual costs (2 years, 10%)		
Amortised capital	£651,400	£461 000
O&M	£290 000	£913 300
Total	£941 400	£1 374 000

### 7.8.3 Zeolites

Zeolites can be used for the removal of ammonia or toxic metals such as cadmium from waste waters. They are made from tetrahedral molecules of hydrated alumino-silicates containing sodium, potassium, magnesium and calcium ions, and comprise a three-dimensional lattice which is capable of adsorbing ions from solution. Conventional ion exchange resins developed for water treatment may select calcium and magnesium ions in preference to the target pollutant and are expensive to use.

In a typical plant influent trickles down through a 1 m deep bed containing graded zeolite with a particle size of 1 to 3 mm. When the bed is saturated, the feed is stopped and a suitable regenerant is applied to remove the target pollutant. This will create a concentrated effluent stream that will require further treatment. A typical plant has two beds, one in abatement mode and the other in regeneration mode.

### 7.8.4 Membranes/Reverse Osmosis

Membrane treatment involves the passage of the waste water through a membrane which acts as a barrier to suspended particles and some dissolved substances. The technique may be run cross-flow, i.e the flow of treated water through the membrane is perpendicular to the flow of feed water. The impurities remain in the feed water, which reduces in volume through the plant, giving a concentrated waste stream (the concentrate) at the outlet. The treated effluent which has passed through the membrane, the permeate, exits the membrane vessel separately.

A range of membranes are available, which gives a degree of flexibility for treatment options. Membranes are defined according to the size of the particle or molecule which is prevented from passing through the membrane. Where membranes are acting as barriers to dissolved molecules, the membrane can be classified according to its molecular weight cut off point (MWCO), i.e the approximate molecular weight above which molecules cannot pass through the membrane. Table 7.17 shows situations in which such techniques can be applied.

**Table 7.17 Technique application ranges for a number of different types of membrane**

	Pore size (µm)	MWCO	Application
Microfiltration	10.1 to 1	>100,000	Particles
Ultrafiltration	0.001 to 0.1	50,000 to 100,000	Particles + large dissolved molecules
Nanofiltration	0.001 to 0.01	200 to 10,000	Dissolved medium molecules
Reverse Osmosis	<0.001	<200	Most dissolved molecules

Nanofiltration membranes are appropriate for the removal of some larger organic molecules and the removal of multivalent ions. A surface charge present on the membrane is the main factor in this latter application.

Membranes are available in a range of materials and configurations. The optimum for a particular application will depend on the nature of the waste water as the materials have varying resistances to degradation by dissolved substances.

Polyamide based membranes and the nanofiltration range constructed as thin film composites are normally superior to cellulose acetate based membranes for removal of trace organic molecules.

Membrane treatment produces a waste stream of approximately 10% of the feed volume, in which the target substances will be present at levels approximately 10 times their concentration in the waste water. The disposal of this concentrate should be assessed. Where the substances removed are organic, the concentration stage can reduce volumes and improve reaction kinetics for subsequent oxidative destruction processes. Where the substances removed are inorganic, the concentration stage could be used as part of a recovery process. In both cases, the permeate water from a membrane process could potentially be re-used or recycled in the industrial process, thus reducing water consumption.

As the concentration of the feed water increases through the plant, and particularly at the interface with the membrane, there can be a tendency for fouling to occur. This is reduced primarily by designing the plant to maintain high velocities and turbulence at the membrane surface, but it is sometimes necessary to dose anti-scaling compounds to the feed waste water. These are non-toxic, have been used for drinking water and would not significantly increase the problem of disposal of the concentrate stream.

Table 7.18 lists some removals of target substances that have been reported in the literature or estimated from known removals of similar materials.

**Table 7.18** Reported removal rates for membranes for a number of pollutants

Compound	Type	Removal (%)
Inorganic mercury	NF	>90 *
Organic mercury	NF	>90 *
Cadmium and its compounds	NF	>90
gamma hexachlorocyclohexane	RO	99
DDT	RO	100
Aldrin	RO	100
Dieldrin	RO	100
Carbon tetrachloride	NF	96
Dichlorvos	RO	98
1,2-dichloroethane	NF	71
trichlorobenzene	NF	96
atrazine	RO	84 to 97
	NF	>70
simazine	RO	95
trifluralin	RO	99
fenitrothion	RO	99
azinphos-methyl	RO	98
malathion	RO	99
perchloroethylene	NF	90 to 92

\* Estimate from knowledge of similar compounds

Current R&D is examining the use of 'dynamic membranes'. These are formed *in situ* by the deposition of chemicals, dosed into the water, on a supporting matrix. This matrix is normally a ceramic microfilter. The deposited chemicals act as a membrane due to their chemical repulsion of the target pollutant. Dynamic membranes may therefore be considered when techniques are being selected in the future.

Experimental work on the removal of some organic compounds from waste water has indicated that some adsorption onto the membrane occurs. This might have implications for the life of the membrane and would need to be assessed for each chemical/membrane combination.

Some membrane materials are damaged by halogens, such as chlorine. If chlorine is present in the waste water, then the membrane choice should take this into account, or the chlorine should be removed.

### 7.8.5 Ceramic Membranes

Ceramic membranes have a rigid structure and are produced from sintered alumina or zirconia. Membrane pore sizes can be manipulated for a particular purpose by varying the cycles of the sintering process. Their rigidity allows construction to be based on tubes or monoliths. Typically a filter unit will comprise a housing and several of the sintered units. The waste water is fed down the centre of the sintered tubes and the filtrate collected from the outside.

The main advantages are conferred by the rigid structure and stability of the sintered materials. The membranes can be heated, back washed and cleaned using solvents. Furthermore the filters exhibit a much greater resistance to chemicals and are much less susceptible to blocking by suspended solids than are conventional membranes. In some situations it is possible to pass cleaning sponges down the tubes to clear any blockages that may occur

The major disadvantage of ceramic membranes is that they cannot be made with the same low ratios of volume to surface area consequently the space required for the filter units is much larger. They are also much more brittle than polymer membranes and vibration should be considered as a potential cause of damage.

Another key limitation on their application is that the membrane production methods will not allow reliable reverse osmosis or nanofiltration units to be produced. However, hybrid systems can be developed by which ceramic membranes are produced and polymer membranes mounted on their surface. The combined membrane approach may enable RO or nanofiltration to be applied but also tends to exhibit the weaknesses of both membrane types.

## Costs

Simple production and engineering should deliver low cost units but this is not always the case. The cost of the unit is driven by the application market and their use for the recovery of fine chemicals and high value products has increased the unit price. Current costs are:

Ceramic membranes	£1500/m <sup>2</sup>
NF polymermembrane	£10/m <sup>2</sup>

The main cost component of the filter unit may be the housing. In a recent study a pilot scale unit comprised membrane units of £450 and the housing was £1100. Cheaper units can be produced if the housing is PVC but this substitution may itself confer limitations in the use of the system.

Reported costs from the water industry vary widely, making prediction of costs difficult. The combined capital and operating costs for NF membranes is typically between 17p/m<sup>3</sup> treated and 45p/m<sup>3</sup> treated. Factors which increase the costs are particulates in the water, which require pre-treatment, and the propensity of the waste water to foul the membrane surface biologically or with scale.

Power costs are reported as 0.7 kWh/m<sup>3</sup> treated assuming a pressure of 20 bar. The cost will be a third of this for nanofiltration.

### 7.8.6 Ion exchange

Ion exchange units consist of a resin bed or beds designed to remove cation (positively charged ions) or anions (negatively charged ions) from waste water. The waste water flows through exchange beds and the target pollutants bind to the bed material, displacing comparatively innocuous ions. The advantages of ion exchange are that water savings are significant, energy consumption is relatively low, and the technique works well on dilute waste waters. The

disadvantages are high costs for chemicals, labour and maintenance. In addition, capital costs are relatively high and the technique is not capable of producing a highly concentrated stream for recycling. It is also necessary to feed a low turbidity water to the ion exchange plant so as not to blind the bed.

Periodically, the resins beds must be chemically treated to remove the absorbed pollutants. For this reason, ion exchange units are usually installed in parallel. The waste water is diverted through the second unit while the first one is being regenerated. The material removed from the resin beds often can be used in process baths.

Regeneration is usually based on the passage of sodium chloride brine through the resin, normally in the opposite direction to the flow of waste water. This counter-current regeneration is important in maximising the efficiency of regeneration and in minimising the pollutant load in the treated effluent. During regeneration, the resin bed is prevented from fluidising by one of a range of techniques. This is necessary to achieve full counter-current regeneration.

A typical regeneration would use a 4 to 10% w/v sodium chloride solution, with the total sodium chloride input to the ion exchange column being 100-200 g l<sup>-1</sup> resin. The appropriate conditions would be identified by pre-design tests and commissioning trials.

Removal of cations from waste water by ion exchange can be achieved by de-alkalisation resins. These replace cations with H<sup>+</sup> ions. These ions then react with bicarbonate and carbonate in the water, producing CO<sub>2</sub> gas.

The waste regenerant will contain significant concentrations of the target pollutant. This stream will typically be about 2 to 4% of the treated waste water volume. The disposal of the waste regenerant is a major process consideration. The ion exchange treated water would be potentially suitable for recycling or re-use.

The following compounds can be removed from waste water by ion-base-exchange:

- cadmium and its compounds;
- inorganic mercury;
- organic mercury (98% removal).

Ion exchange resins, as well as exchanging ions, often have a significant capacity for the adsorption of organic compounds, particularly those molecules with polar properties.

If the target substances are competing for ion exchange sites with other cations in the water this will significantly reduce the capacity of the resin for the target pollutant. If the influent waste water contains an ion which the resin selectively removes at the expense of the target substance, then this ion can displace the target substance from the resin. This displacement may occur after a period of time and may result in higher effluent concentrations of the target substance than were present in the feed.

As the resin becomes exhausted, the concentration of the target substance in the treated water will gradually increase. In order to prevent significant levels being found in the treated water, it would be necessary to allow a safety margin in calculating the regeneration time.

Some base exchange resins can be degraded by the presence of halogens, such as chlorine, in the waste water. In order to maximise the life and performance of the resin, the waste water should be dechlorinated. Data on maximum chlorine levels which can be tolerated are available from resin suppliers.

## **7.9 Cost of waste water techniques**

Some indicative costs for waste water techniques are summarised in Table 7.19. Costs have been calculated using the equations provided in the preceding sections and using the assumptions listed in the table.

## **7.10 Conclusions**

Before any waste water technique is selected and applied it is vital that waste water arisings and water use in the process and, if relevant, the wider site are accurately characterised. This will allow opportunities for prevention and minimisation to be identified. It will also enable problematical streams to be isolated and downstream treatment to be optimised in terms of both removal efficiencies and cost.

Biological treatment, whether applied on-site or after discharge to sewer, is widely applied in the sector as the main treatment step. A well managed biological plant can deal with a wide range of waste water streams and their use is well understood.

Recent innovations in waste water techniques have largely come in the area of, what this study terms, special treatment that can be applied to problematical streams. Whilst special techniques have been developed to deal with most waste waters the selection of the optimum one to use can be difficult with quite small variations in the waste stream's characteristics making a significant difference to the viability of a particular technique.



**Table 7.19 Indicative costs for waste water techniques.**

Technique	Costs (1996 £)			Includes	Excludes
	Capital	Annualised <sup>(1)</sup>	Annual operating		
Powdered activated carbon	£3400	£554	£768	<ul style="list-style-type: none"> <li>• Dosing equipment</li> <li>• Powdered activated carbon dosed at 20 mg/l costing £500/tonne</li> <li>• A daily flow of 100 m<sup>3</sup>/day</li> <li>• Sludge (5% solids) disposal costs of £20/tonne to landfill</li> </ul>	<ul style="list-style-type: none"> <li>• Labour</li> <li>• Maintenance</li> </ul>
Granular activated carbon	£19100	£3113	£3100	<ul style="list-style-type: none"> <li>• Cost of GAC plant</li> <li>• Cost of GAC with a density of 450 kg/m<sup>3</sup> at £1500/tonne</li> <li>• A daily flow of 100 m<sup>3</sup>/day</li> <li>• An empty bed contact time of 15 minutes</li> <li>• Regeneration every 2 months</li> <li>• A 10% loss of GAC each regeneration</li> <li>• Regeneration costs of £800/tonne</li> </ul>	<ul style="list-style-type: none"> <li>• Labour</li> <li>• Maintenance</li> </ul>
Chemical coagulation	£121000	£19723	£2571	<ul style="list-style-type: none"> <li>• Sedimentation tank</li> <li>• Chemical plant</li> <li>• Coagulant (ferric dosed at 12 mg/l)</li> <li>• A flow of 100 m<sup>3</sup>/day</li> </ul>	<ul style="list-style-type: none"> <li>• Sludge disposal</li> <li>• pH adjustment chemicals</li> <li>• Maintenance</li> <li>• Labour</li> </ul>
Ozone	£148000	£24124	£5800	<ul style="list-style-type: none"> <li>• Ozone generator</li> <li>• Building</li> <li>• Contact tank</li> <li>• Contact time of 15 minutes</li> <li>• A daily flow of 100 m<sup>3</sup>/day</li> <li>• Ozone dose of 68 mg/l</li> <li>• Electricity costs at 4p/Kwh</li> <li>• Cooling water costs at 50p/m<sup>3</sup></li> </ul>	<ul style="list-style-type: none"> <li>• Maintenance</li> <li>• Labour</li> </ul>
Air stripping	£10500	£1724	£12	<ul style="list-style-type: none"> <li>• Tower</li> <li>• Blower</li> <li>• Packing at £250/m<sup>3</sup></li> <li>• A daily flow of 100m<sup>3</sup>/day</li> <li>• Electricity costs of 4p/Kwh</li> </ul>	<ul style="list-style-type: none"> <li>• Maintenance</li> <li>• Labour</li> </ul>

Notes: <sup>(1)</sup> Annualised costs calculated on basis of a 10% discount rate for cost of capital for 10 years



## 8. LAND TECHNIQUES

The identification and application of techniques for preventing, minimising and controlling releases to land should reflect the waste management hierarchy. Thus:

- waste arisings should be prevented at source. Techniques could include the use of waste minimisation programmes to identify waste prevention opportunities (see Section 4.3.1 on Management Techniques);
- where waste arisings cannot be prevented they should be characterised and classified. This should occur at the earliest possible stage in the process and should cover both composition and quantity. Waste characterisation helps identify recycle/reuse opportunities and, where these cannot be applied, allows the development of a suitable programme for handling, storing and disposing of the waste;
- recycled or reused opportunities can be identified via a waste minimisation programme. It should be borne in mind that recycling opportunities are not confined to the process and other on-site or off-site opportunities should be explored. It may be necessary to separate some wastestreams in order to maximise recycle/reuse opportunities. The potential for environmental releases from separation techniques should not be overlooked;
- a system should be in place to monitor waste arisings on site. This would allow trends to be identified and underpin waste minimisation programmes and disposal practices. The amount of information collected on each waste stream will depend upon its hazardous properties. It would not be expected that as much detail would be collected on inert or non-hazardous wastes as would be the case for hazardous wastes;
- a system should be in place to manage waste arisings. This should cover the use of appropriate labelling, storage containers, storage areas, handling, transportation and disposal;
- the main disposal options (techniques) include incineration, landfill and land application of sludges. More specialised techniques may be required for certain wastes, for example, solidification, encapsulation and composting.



## 9. INNOVATIVE TECHNIQUES

A number of innovations under development for application in organic chemical processes are designed to lead to better process control and higher product quality and consistency. Most of these developments will also lead to increases in overall resource efficiency and hence reduced overall environmental impact.

Developments are summarised below in terms of:

- management techniques;
- process techniques;
- abatement techniques.

### 9.1 MANAGEMENT TECHNIQUES

#### 9.1.1 Behavioural science

A development in the Safety area with direct and obvious consequences for dealing with environmental issues is the involvement by BASF of behavioural scientists over a three year period at their Seal Sands site to help improve site safety. The overall exercise concentrated on shop-floor workers observing their peer groups at work and suggesting improvements. This approach had obvious advantages in getting worker buy in and highlights the importance of the social considerations in effective introduction of improved management systems and practices.

### 9.2 PROCESS TECHNIQUES

#### 9.2.1 Continuous processing

There are, for example, a number of advantages to be gained in moving from batch to continuous processing as was introduced in the 1960s for sulphonation reactions in surfactant production. The continuous film reactors used combined increased product quality and reduced energy use and a reduced reactor cleaning and other start up and shut down wastes. An interesting development in this area is the concept of the mini-reactor, a small scale process run continuously on a small scale. There is still some debate about the overall economics of such systems (Koch 1997) but it has proceeded to the industrial trial stage with promising results. More speculative and very much at the laboratory prototype research stage is the concept of the micro-reactor. This involves using use of a small reactor cell with a capacity of only a few millilitres and a continuous flow system.

#### 9.2.2 Hybridisation of unit processes

One of the most significant and well developed areas is that of the combination or hybridisation of unit processes. A major advantage of these combined operations is a dramatic reduction in capital expenditure but they also offer reduction of by-product formation and the potential to

improve the yields from low equilibrium reactions. One example is the production of ethers such as methyl t-butyl ether by reactive distillation. In this case the preferred operating range of the catalyst corresponds to that for the distillation of the product from the reactants and inerts so the process also provides savings in energy. Catalytic membranes in which the catalyst forms part of a separation membrane which can separate reactants from products is another example of a hybrid process which can lead to improved energy efficiency and improved yields.

### 9.2.3 Computer simulation and control

Another area of significant development with important implications is that of computer simulation and control. The development of systems to allow simulation of dynamic processes is important because it allows scope for the optimisation of batch processes against various criteria. Such models have been applied, for example to optimise solvent recovery by batch distillation and reduced organic wastes by 88% (Ahmad 1995).

A recent output from the Energy Efficiency Best Practice Programme (Good Practice Guide 215 reducing energy costs in industry with advanced computing and control) contains some particularly useful guidance information on available techniques and the circumstances under which each might be considered (ETBPP 1997a). Of relevance to the chemical industry is the 8% saving in energy at the BP Hull site resulting from using a site-wide energy management information system. In a similar vein the integration of computer aided plant and process design with process simulation software provides the scope for earlier optimisation of process efficiency with obvious environmental improvement consequences.

### 9.2.4 Catalytic processes

Although catalysis often uses less toxic chemicals and has lower energy demands than standard organic chemistry techniques they have not been widely employed in industrial processes. A recent application of catalysis to the synthesis of a key intermediate for a new anti-arthritis drug however demonstrates its potential. The previous no-catalytic process involved a five step synthesis involving chlorosulphonyl isocyanate, a gas that is 100 times more toxic than methyl isocyanate, the gas involved in the Bhopal incident. The new catalytic process is a single step, avoids this toxic gas and has reduced production costs by 30-40% (Pharma Visions 1997).

### 9.2.5 Supercritical fluids

Research at the University of North Carolina has demonstrated the potential for the use of supercritical carbon dioxide as the solvent for dispersion polymerisation reactions that are normally conducted in water. This approach used a special free-radical initiator and polymeric stabiliser. It offers the potential to eliminate waste waters containing low levels of monomer and occasional off specification mixtures that pose special disposal problems. The use of supercritical fluids are not without their own rather demanding engineering problems but they may find use in specialist product areas in the future.

## **9.3 ABATEMENT TECHNIQUES**

### **9.3.1 Plasma techniques**

A plasma is an excited gas in which molecules have become dissociated. Excitation can be caused by direct current, radio waves or microwaves. The plasma then provides the energy which can breakdown the VOCs into carbon dioxide and water (Akehurst 1997).

Sharratt (1996) reports that in laboratory tests acetone, toluene and trichloroethylene have all been reduced by more than 99% and butanone by more than 95%. A number of further research steps are noted that will be required before the technique can be tested under real conditions. For example, developing a durable system and stabilising the microwave source across all power levels.

### **9.3.2 Corona techniques**

The USEPA (1995) reports that corona discharges can be used to destroy VOCs. Corona discharges utilise a high voltage/low current electrical discharge to facilitate the breakdown of the VOC. Dielectric packed bed reactors and nanosecond pulse coronas are reported to offer the greatest potential for the development of an available technique. The study cautions that ozone generation may cause problems.

### **9.3.3 Polymer membranes**

Polymer membranes work on the principle that certain molecules preferentially pass through them whilst others do not. If the concentration of the VOC in the gas stream is low then a high vacuum will be required to draw the VOC molecules through the membrane.

Polymer membranes have not been demonstrated as stand alone primary abatement techniques because most polymer membranes have:

- low transmission fluxes meaning that very large areas of membrane are needed to deal with the flows typical of the chemical industry; and
- poor selectivity for the most commonly used solvents.

Until these problems are adequately resolved, polymer membranes will remain of peripheral interest.





## 10. BENCHMARK RELEASE LEVELS

Benchmark release levels are intended to be indicators of the amount of a chemical that can be expected to be released from a process that is employing BAT. These values can, in theory, provide a rapid way of judging whether BAT is being applied in a given situation. However, this sector is characterised by a significant diversity in processes, raw materials, reaction chemistries and products. This makes it particularly difficult to derive uniform release levels that are applicable in all situations. Even when comparable processes can be identified such levels should only be regarded as a check on overall performance. Too much attention paid to this single "end-of pipe" factor can draw attention away from actions to prevent and minimise releases which should be happening further up stream.

Various dimensional units are applied to such levels such as concentration units (mass of chemical per unit of release medium (air, water or solid)) or flux or load units of chemical (mass per unit of time of process operation, typically kg per hour or per day) or in terms of process efficiency (mass per unit of production, either actual production or plant capacity).

Problems with the application of achievable release values in the sector are briefly outlined in this section together with recommendations on potential revisions to the current levels and approaches.

### 10.1 Current position

The current Guidance Notes provide concentration values for some substances in  $\text{mg}/\text{m}^3$  for air and  $\text{mg l}^{-1}$  for water that represent "release levels that are achievable by all new processes using BAT". The guidance emphasises that they should not be construed as uniform release levels but should take account of site specific factors "which may require more stringent" limits to be set.

The current Guides note that total mass released or mass per unit of production may be more appropriate for VOCs. The German TA Luft system has adopted a joint concentration/mass approach and parameters can have different concentration limits for different mass release rates e.g. "Total dust"  $>500 \text{ g h}^{-1}$  has a limit of  $50 \text{ mg}/\text{m}^3$  while  $<500 \text{ g h}^{-1}$  has a limit of  $150 \text{ mg}/\text{m}^3$ .

There are several potential problems with the current approach to applying benchmark release levels in this sector. The main ones are as follows:

- the steady state levels quoted may be much more difficult to achieve with the intermittent releases that are characteristic of the batch production processes prevalent in this sector;
- levels quoted may be low but if the release has a high volume the release may involve a large amount of material;
- levels quoted in the literature and by manufacturers are usually based on a simple gas stream containing a single VOC. In practice, gas streams in this sector are likely to

contain many VOCs, moisture, particulates and acid gases, all of which may prevent the optimum release level being achieved;

- there are a wide range of reaction chemistries, raw materials, products and releases in the sector.

## 10.2 Possible approaches

### 10.2.1 Intermittent releases

The priority for process operators should be to prevent and minimise all releases. Within these constraints, however, there is a reasonable case for allowing higher short term release levels since these are likely to be less harmful than longer term releases. It may also be more difficult to achieve short term release levels by the application of affordable techniques. It is therefore necessary to identify a suitable trade off between the higher levels, the time period of release and the potential effects.

Harm from exposure to a given chemical will generally increase with both the concentration of the chemical and the exposure period but there is no general relationship between exposure concentration, exposure period and harm so general guidance is not possible. The following is offered as a guide to some of the issues likely to be involved and the data that could be used to help reach decisions.

The first issues to consider in relation to a short term release are its composition, magnitude, duration and frequency. These can then be compared with guidance levels provided in the Agency's Technical Guidance Note E1 (HMSO 1997).

If the short term concentration for a given release is below a guidance level provided in E1, and there are no ways of avoiding or otherwise minimising the release, then there is no reason to consider other techniques to reduce it further. If the level is above the E1 guidance level then the key points to consider will be

- the magnitude of the difference;
- the duration of the release;
- the nature of the toxic response and target associated with substances involved.

As noted above it is impossible to give general guidance on this issue other than the observation that the larger the difference involved the more attention should be devoted to it. In some cases there may be other data that can be drawn on to help make decisions. For example, there are, in the case of air, short term exposure limits, mostly for worker exposure, that can be consulted (HSE 1997). The Dutch have also produced some guidance for releases resulting from either batch reactions or start-up conditions (NeR 1992).

Many short term releases to air from chemical processes will be primarily a hazard to process workers and the Occupational Exposure Limits (OELs) published by the Health and Safety Executive (HSE) can be referred to for guidance. As a first rule of thumb if the workers are likely to be directly exposed and if they are sufficiently well protected by the occupational level then this is probably a satisfactory basis for protection of the environment. These occupational

values often have both short term - 15 minute - exposure period values and longer term eight hour time weighted average values. The ratio of these values is typically in the range of 2-3 and in the absence of other more specific information this ratio could be used as a factor to allow increases in the long term achievable release level or in the threshold level of releases above which this level should apply. But the use of such factors should be checked with appropriate experts in the field.

### 10.2.2 Long term releases

The main potential problem with long term release levels is that low levels of a compound released over long periods may represent large aggregate amounts of material that is both wasteful and potentially harmful to the environment. A release amount per unit of product would provide a more appropriate measure to monitor this aspect of process performance but it would, for this sector, be very difficult to derive because of the emphasis on batch operations.

Several countries have followed the TA Luft (1986) approach of using guideline concentration limits for discharges above a given flux level for emissions to air. This approach is easier to apply to continuous production plants with steady discharges where the flow rate of the discharge can be more readily measured or estimated.

Probably the best approach for this sector is to use achievable release values expressed as concentrations, load reductions or as loads per time unit as a guide but also to regard environmental performance indicators (EPIs) such as resource use per unit of production as a component of BAT for the management of such processes. It is unlikely that EPIs could be used as the basis for regulation but in many cases they may be a powerful managerial tool for monitoring process performance and prioritising process unit areas, batches and products that have a disproportionate impact on resource use and releases. Despite the diversity of the sector it may be possible to benchmark some processes using EPIs; although process specific factors would have to be considered carefully.

## 10.3 Approaches adopted by other countries and organizations

Many organisations and countries, notably Germany and the USA, have established guideline or standard emission limits for the releases of chemicals from the chemical industry and many of these values have been presented in the existing CIGNs. Such values from other countries are often much less simple than they appear at first sight for a variety of reasons. These reasons include:

- they only apply to new plant;
- apply to plant involved in the production of a particular substance;
- are guideline values and considerable flexibility applies in their practical implementation;
- are target values which are frequently not achieved in practice; and
- apply, and can only be complied with, as part of a suit of conditions.

It follows that care is needed in the application of values derived from other country's regulations. Nevertheless this is probably the most robust source of information from which to derive benchmark release levels.

Care has also to be exercised in the use of these values because once a value is published it often becomes the source for other values and the exercise becomes circular. This has happened, for example with the Irish emission values which seem to be those previously published by HMIP, many of which have the same values as those given by TA Luft.

These TA Luft values have been widely copied by other countries, including in some cases the UK, but they are now over ten years old and probably in need of review. The Environment Agency has already taken steps to move beyond the values used in TA Luft for specific IPC sectors. Despite this TA Luft remains the most robust source of information on technology based limits and careful consideration is required to justify moving beyond its requirements.

The other potential source of benchmark values would be measured values from sites. There will be obvious problems of data quality associated with this approach but the biggest and probably insurmountable problem for this sector is the wide variety of detailed process configurations and conditions involved. Experience indicates that the data available, for example that in the CRI, and the variety of processes involved make this impractical.

Alternatively standard emission factors could be derived. An exercise of this kind has been undertaken in the USA which has resulted in the development and publication of the AP-42 "compilation of air pollutant emission factors" (USEPA 1991). AP-42 contains significant amounts of information, 16 reports are available covering 14 chemical substances and produced over a five year period. Clearly an input of very considerable resource.

The specific information relating to the organic chemical process industry sector comprise 29 sections, 15 of which are still in draft. Potential sections of interest to this study relate to synthetic fibres and soap and detergent manufacture. Of these 29 sections, a number were first published in the early 1980s and are therefore of variable reliability since many changes are likely to have happened over nearly 20 years. The information contained in some of these documents has been reviewed and it has been concluded that it is too variable to be of value in this study.

### **10.3.1 Releases to air**

There now seems to be very widespread adoption of the German TA Luft standards and approach for the release of substances to air. The basis of this thinking is to assign a given chemical to a general class and establish a limit for the total release of this class of substance above a given flux level. The regulations are quite complex and deal with many special cases. They also contain additional detailed requirements, for example, that 97% of all half hourly means shall not exceed 120% of the established mass concentration. Taking just the simple limit values, Table 10.1 illustrates this concept with values taken from the Irish regulations (Irish EPA 1996).

The TA-Luft regulations contain lists of chemicals assigned to classes and a more recent document provides a procedure for classifying new substances (UBA 1997). This classification

procedure is based on a substance's established or suspected carcinogenicity and work place limits or its classification under EU Existing Substances Regulations.

**Table 10.1 Emission limit values for general emissions to air (Irish EPA 1996)**

Constituent Group or Parameter	Class	Mass flow threshold for ELV	Emission limit value (mg/m <sup>3</sup> )
Carcinogenic Substances	TA Luft I	>0.5 g hr <sup>-1</sup>	0.1
	TA Luft II	>5.0 g hr <sup>-1</sup>	1.0
	TA Luft III	>25.0 g hr <sup>-1</sup>	5.0
	Substances other than those above which have R45 designation	>0.5 kg hr <sup>-1</sup>	5.0
Inorganic dust particles	TA Luft I	>1 g hr <sup>-1</sup>	0.2
	TA Luft II	>5 g hr <sup>-1</sup>	1.0
	TA Luft III	>25 g hr <sup>-1</sup>	5.0
Vaporous or gaseous inorganic substances	TA Luft I	>10 g hr <sup>-1</sup>	1
	TA Luft II	>50 g hr <sup>-1</sup>	5
	TA Luft III	>0.3 kg hr <sup>-1</sup>	30
	TA Luft IV	>5.0 kg hr <sup>-1</sup>	500
Organic substances with POCP	UK AEA I	>0.5 kg hr <sup>-1</sup>	20
	UK AEA II	>2.0 kg hr <sup>-1</sup>	50
Organic substances (Note 1)	TA Luft I	>0.1 kg hr <sup>-1</sup>	20
	TA Luft II	>2.0 kg hr <sup>-1</sup>	100
	TA Luft III	>3.0 kg hr <sup>-1</sup>	150
General dusts		<0.5 kg hr <sup>-1</sup>	150
		>0.5 kg hr <sup>-1</sup>	20
Pharmaceutical and pesticide dust - as active ingredient		>1 g hr <sup>-1</sup>	0.15
Fugitive emissions			Note 2

Notes:

- 1 Where organic substances of several classes are present, in addition to the above limit, the sum of Classes 1 and 2 shall not exceed the Class 2 limit and the sum of Classes 1, 2 and 3 shall not exceed the Class 3 limit etc.
- 2 Fugitive solvent emissions should comply with the requirements of the proposed EU Solvent Directive

The Dutch have adopted similar emission guideline values but have also provided guidance for short term emissions, occurring, for example during start up or for batch operations. The guidance given is built around mass flow check values (CV), see Table 10.2 (NeR 1992).

**Table 10.2 Dutch mass flow check values for short term releases**

Chemical class	Flux limit (g hr <sup>-1</sup> )	Emission concentration limit (mg/m <sup>3</sup> )	Mass flow CV
Carcinogen 1	0.5	0.1	0.5
Carcinogen 2	5	1	5
Carcinogen 3	25	5	25
General particulates	<500	50	1000
General particulates	>500	10 filter or 25/50	1000
Inorganic particulates 1	1	0.2	1
Inorganic particulates 2	5	1	5
Inorganic particulates 3	25	5	25
Inorganic gas 1	10	1	10
Inorganic gas 2	50	5	50
Inorganic gas 3	300	30	300
Inorganic gas 4	5000	200	5000
Organic gas 1	100	20	100
Organic gas 2	2000	100	2000
Organic gas 3	3000	150	3000
Organic particulate 1	100	20	100
Organic particulate 2	2000	100	250
Organic particulate 3	3000	150	250

For batch processes a number of constituent units e.g. storage tanks, reactors etc. can be treated as a single source if releases from them can be fed to a single treatment facility. It would then be considered BAT if the total aggregated residual emission was less than 1000 times the CV in g yr<sup>-1</sup>. In the permit to operate this would be presented either as a concentration limit or a mass flow with a duration equivalent to the operation of the batch.

Irregular emissions that are less than 100 times the CV in g yr<sup>-1</sup> can be ignored in the design of the plant and, by implication presumably in the determination of BAT.

Parcom draft guidance (UBA 1994) for the speciality organic chemical industry provides some data on limits for total solvent losses. For sites using less than 100 tonnes of solvent per year less than 4% of the total use should be released to the atmosphere, if only one solvent is being used. This figure can increase to 8% if more than one solvent is used. For large users, i.e. more than 1000 tonnes per year, smaller percentage losses are expected 0.4% for single solvent single product, 0.8% for single-product, multi-solvent and 4.0% for multi-solvent, multi-product sites. In order to ensure there is no transfer to water to reduce atmospheric releases they also propose that water discharges should never be more than 1% of the atmospheric release. For users of between 100-1000 tonnes per year extrapolation should be used between the less than 100 and more than 1000 tonnes per year figures, respectively.

### 10.3.2 Releases to water

A number of countries, notably Germany and the USA, and international organizations, including the Paris Commission (Parcom), Helsinki Commission (Helcom) and the Rhine Commission, have or are developing binding or guide values for discharges to water.

The approach to issuing of consents in Germany for discharges from chemical processes is complex and multi-faceted so the final consents which are built around aggregated parameters like AOX (total adsorbable organic halogen - a general measure of total halogenated organic chemicals) and COD (chemical oxygen demand) cannot be readily transferred to other regulatory systems.

Process operators are required to generate a waste water register covering the sources, quantity and composition of all waste streams. Prior to the issue of a consent the process operator is expected to conduct a waste water minimisation exercise. The discharges are then consented in terms of COD (or increasingly total organic carbon - TOC), adsorbable organic halogens (AOX), nitrogen, heavy metals (if present), phosphorus and fish toxicity. The values are summarised in Table 10.3.

Experience in Germany of COD values from chemical plants shows the problems with trying to establish a limit for this parameter, achievable release levels varied from 40 mg l<sup>-1</sup> to over 300 mg l<sup>-1</sup> for sites utilising similar treatment techniques. Similarly, the variations in COD releases in relation to production were substantial, ranging from 0.3-35 kg COD/tonne product. The reduction standard that is used for COD applies to all in-process measures not just the final biological treatment plant (UBA 1994).

**Table 10.3 Minimum standards applied in Germany to waste water discharges**

Parameter	Measure required
COD	90% reduction for waste waters in the range 750-50,000 mg/l
Phosphorus	2 mg l <sup>-1</sup>
Total N	50 mg l <sup>-1</sup> or 25% of total load
AOX	1 mg l <sup>-1</sup> or 20 mg kg <sup>-1</sup> of product
Fish toxicity	No acute fish toxicity when waste water at point of discharge is diluted two-fold

AOX is not a parameter that has been used traditionally in the UK. In Germany the limits are currently 1 mg l<sup>-1</sup> or 20 g AOX/tonne of product. Parcom in their draft emission limits propose 0.1 mg l<sup>-1</sup>. Experience in Germany is that the achievable limit is highly dependant on the nature of the processes involved but that AOX does provide a good aggregate measure of treatment performance. The German authorities are presently discussing with industry a revision of the AOX limits.

For the pesticide industry, the United States Environmental Protection Agency (USEPA) has developed a series of "New source performance standards". These standards provide effluent limits for active ingredients in terms of efficiency of the pollution prevention, specific effluent

concentration limits for priority pollutants and gross pollution efficiency measures for COD, BOD, pH and suspended solids. The limits cover 71 pesticides and 27 priority pollutants. Examples of the limits are given in Table 10.4 below (USEPA 1993).

**Table 10.4 USEPA New source performance standards for the pesticide industry**

Chemical	Daily maximum limit	Monthly average limit
COD	9.36 mg kg <sup>-1</sup> product	6.48 mg kg <sup>-1</sup> product
BOD-5	5.33 mg kg <sup>-1</sup> product	1.15 mg kg <sup>-1</sup> product
Total suspended solids	4.39 mg kg <sup>-1</sup> product	1.30 mg kg <sup>-1</sup> product
pH	6-9	6-9
Alachlor	3.74 mg kg <sup>-1</sup> product	1.11 mg kg <sup>-1</sup> product
Carbaryl	1.18 mg kg <sup>-1</sup> product	0.524 mg kg <sup>-1</sup> product
Fenarimol	102 mg kg <sup>-1</sup> product	36.1 mg kg <sup>-1</sup> product
1,4-dichlorobenzene	380 µg l <sup>-1</sup>	142 µg l <sup>-1</sup>
toluene	74 µg l <sup>-1</sup>	28 µg l <sup>-1</sup>
1,1,1-trichloroethane	59 µg l <sup>-1</sup>	22 µg l <sup>-1</sup>

These values have been established as uniform national emission standards.

Guidelines drafted by Parcom relating to BAT for the biocide industry are in the main significantly more stringent than the values given by EPA in that they expect that the total active ingredient in the discharge from these plants should be in the range 0.1-1.0 mg per tonne of product and that these values will typically result in levels in the effluent in the range 1-10 µg l<sup>-1</sup> (UBA 1994).

Parcom has also produced draft emission limits for the organic chemicals sector which can also be regarded as benchmark values for processes using these substances. The draft Parcom limits are based on the final treated discharge from a treatment works and on concentrations in individual (tributary) waste streams before they are combined and sent for central treatment. These draft values were originally derived in 1994. No subsequent progress has been made on their development and it is by no means certain that they will be adopted in this format (UBA 1994). The draft release levels as they stood in 1994 can be summarised as:

**(a) Discharges from central treatment**

For direct discharges to surface waters:

- the COD concentration should not exceed 125 mg l<sup>-1</sup> and shall not exceed 200 mg l<sup>-1</sup>;
- the BOD concentration should not exceed 25 mg l<sup>-1</sup>;

The concentration of organohalogenes shall not exceed 0.1 mg l<sup>-1</sup>. This concentration can be expressed as one of the following three options:

- AOX (adsorbable organo-halogens);
- EOX (extractable organo-halogens);



- where it has been possible to identify all individual hazardous AOX/EOX contributants, the sum of these contributants.

For on-site final treatment plants with influents over 10 000 pe, discharging directly into surface waters that is, or may influence, an area sensitive to nutrients:

- total phosphorus concentrations should not exceed 2 mg l<sup>-1</sup>;
- total nitrogen concentration should not exceed 15 mg l<sup>-1</sup>.

The total suspended solids concentration:

- shall not exceed 50 mg l<sup>-1</sup> for discharges to surface waters;
- should not exceed 50 mg l<sup>-1</sup> for discharges to sewer.

#### (b) Tributary waste streams

- total organohalogens should not exceed 1.0 mg l<sup>-1</sup> i.e the sum of carbon tetrachloride, chloroform, 1,2-dichloroethane, trichlorobenzenes, trichloroethylene, perchloroethylene, 1,1,1 trichloroethane and dichloromethane;
- total monocyclic aromatic hydrocarbons concentration should be less than 10 mg l<sup>-1</sup> i.e the sum of benzene, toluene, xylenes, cumene, ethyl benzene and styrene;
- copper, nickel, lead and chromium VI should not exceed 0.5 mg l<sup>-1</sup> for each substance individually;
- zinc should not exceed 0.5 mg l<sup>-1</sup> (but this may be more difficult to achieve and the guideline recommended is 2 mg l<sup>-1</sup>).

The use of the word shall suggests a binding limit value whilst the word should suggests a guidance (benchmark) value. An existing Parcom recommendation relating to the Pharmaceutical industry suggests reductions in COD of 75% prior to discharge (Parcom 1992).

The Rhine Commission requires reductions in COD (or TOD) and AOX (or EOX) of 90% prior to discharge. Whilst the Helsinki Commission (HELCOM) has adopted a non-binding approach based on either a 80% reduction in COD (or TOD) or an effluent concentration of less than 250 mg l<sup>-1</sup> prior to discharge. HELCOM has also adopted a similar non-binding approach for AOX based on an 80% reduction or a concentration of less than 1 mg l<sup>-1</sup> prior to discharge (CITEPA 1997).

In addition Japan has set standards for the release of substances to waters as indicated in Table 10.5 (Pers. Com. Yamauchi 1997).

**Table 10.5 Release limits for substances released to waters in Japan**

Toxic substance	Limit	Toxic substance	Limit
Cadmium	0.1 mg l <sup>-1</sup>	Dichloromethane	0.2 mg l <sup>-1</sup>
Cyanide	1 mg l <sup>-1</sup>	Carbon tetrachloride	0.02 mg l <sup>-1</sup>
OP compounds	1 mg l <sup>-1</sup>	1,2 dichloroethane	0.04 mg l <sup>-1</sup>
Lead	0.1 mg l <sup>-1</sup>	1,1 dichloroethylene	0.2 mg l <sup>-1</sup>
Chromium VI	0.5 mg l <sup>-1</sup>	1,1,1 trichloroethane	3 mg l <sup>-1</sup>
Arsenic	0.1 mg l <sup>-1</sup>	1,1,2 trichloroethane	0.06 mg l <sup>-1</sup>
Total mercury	0.005 mg l <sup>-1</sup>	Thiram	0.06 mg l <sup>-1</sup>
Alkyl mercury	Not detectable	Simazine	0.03 mg l <sup>-1</sup>
PCB	0.003 mg l <sup>-1</sup>	Thiobencarb	0.2 mg l <sup>-1</sup>
Trichloroethylene	0.3 mg l <sup>-1</sup>	Benzene	0.1 mg l <sup>-1</sup>
Tetrachloroethylene	0.1 mg l <sup>-1</sup>	Selenium	0.1 mg l <sup>-1</sup>
BOD	160 mg l <sup>-1</sup> and 120 mg l <sup>-1</sup> daily average	Phenols	5 mg l <sup>-1</sup>
COD	160 mg l <sup>-1</sup> and 120 mg l <sup>-1</sup> daily average	Copper	5 mg l <sup>-1</sup>
Nitrogen	120 mg l <sup>-1</sup> and 60 mg l <sup>-1</sup> daily average	Phosphorus	16 mg l <sup>-1</sup> and 8 mg l <sup>-1</sup> daily average

Another source of information for potential benchmarks is EU Directives. There are several limit values in Directives which could be used as the basis for deriving BAT based benchmark release levels. Caution has to be utilised in using these Directive based values, none of which have been derived specifically for discharges from industrial waste water treatment plants. The values of potential interest and their source are summarised in Table 10.6 below.

**Table 10.6 Relevant limit values from EU Directives**

Chemical	Guideline	Source
COD	125 mg l <sup>-1</sup> daily average	91/271/EEC (CEC 1991)
BOD	25 mg l <sup>-1</sup> daily average	91/271/EEC
Suspended solids	35 mg l <sup>-1</sup> daily average	91/271/EEC
Total nitrogen	15 mg l <sup>-1</sup> daily average	91/271/EEC
Total phosphorus	2 mg l <sup>-1</sup> daily average	91/271/EEC
Mercury	0.05 mg l <sup>-1</sup>	84/156/EEC (CEC 1984)
Cadmium	0.2 mg l <sup>-1</sup>	83/513/EEC (CEC 1983)

**Note** The UWWT limits for nutrients only apply to discharges to "sensitive" areas. However, such limits are achievable by BAT and whether they are applicable in a given case or not is a NEEC consideration.

### 10.3.3 Solid waste

Fewer regulations and standards are available relating to solid waste arisings. Parcom guidance on BAT for the biocide industry is that all containers used for storage and transport of active ingredients should be returnable and any solvent rinsings of containers should be retained for future use.

### 10.3.4 Air benchmark values

Table 10.7 gives the values for releases to air collected from the current guidance notes.

This study has not uncovered any information to indicate that the values given in Table 10.7 are no longer appropriate, except for those of oxides of sulphur and oxides of nitrogen, respectively. It is recommended that the existing benchmark release level for these parameters be reduced from the existing  $300 \text{ mg/m}^3$  to a new value of  $200 \text{ mg/m}^3$ . Manufacturers of absorption techniques have indicated that this value would be demanding but could be achieved for new plants, although there may be particular circumstances where this new value cannot be achieved.

For other substances not covered in the Table 10.7 the TA Luft emission values are widely used and there seems to be no reason why they should not form the basis of benchmark values. The values in the TA Luft regulations are guideline emission levels and have to be interpreted in a site specific way to determine other key operating principles such as stack heights and location.

It is proposed that values for guidelines for short term releases are obtained by application of the ratio of the short term (15 minute) OEL to the eight hour OEL to the long term benchmark release level and in the absence of such values a factor of two be used. Release levels above these should be justified by the process operator in terms of their safety and environmental implications.

### 10.3.5 Water benchmark values

Specific guidance is far more difficult to provide for water than for air. The efficiency of a particular application of a technique will depend on the substances concerned and on precise details of the process and the site.

Values do exist from other countries but they often need to be interpreted in the context of the overall approach to emission control adopted; to simply lift and apply the figures could be very misleading. It seems from experience in Germany that BAT including where it is available on site biological effluent treatment should achieve reductions in COD of the order of 90%. But care is needed in applying such a figure simply to the input and output of the treatment plant because up-stream treatment such as chemical oxidation can have a disproportionate effect on the BOD and leave a greater proportion of recalcitrant COD. This will reduce the removal efficiency of the biological stage although still improve the effluent quality. Chemical processes that may be exceptions to this are those involving recalcitrant polar chemicals like EDTA.

**Table 10.7 Benchmark levels for releases to air**

Substance	Process sector					
	Batch processes	Organo-metallics	Sulphonation and nitration	Halogenation	Pesticides	Pharmaceuticals
Active ingredients	0.15				0.15	0.15
Amines (total as DMA)	10			10		
Ammonia	15					
Benzene	5		5	5		
Bromine	10		10	10		
Cadmium and its compounds	0.1					
Carbon disulphide	5					
Carbon monoxide	100		100	100		
Chlorine	10		10	10		
1,2 Dichloroethane	5			5		
Formaldehyde	5			5		
Fluorine and its compounds				5		
Hydrogen bromide	5		5	5		
Hydrogen chloride	10		10	10		
Hydrogen cyanide	2					
Hydrogen fluoride	5		5			
Hydrogen iodide	5		5	5		
Hydrogen sulphide	5					
Iodine	10		10			
Lead and its compounds - total particulate as Pb	4	4				
Lead and its compounds - total non particulate as Pb	20	20				
Mercury and its compounds	0.1					
Nitrobenzene			5			

Substance	Process sector:					
	Batch processes	Organo-metallics	Sulphonation and nitration	Halogenation	Pesticides	Pharmaceuticals
Nitropropane			5			
Organic sulphides and mercaptans	2					
Oxides of sulphur	300		300	300		
Oxides of nitrogen	300		300	300		
Particulate matter	20	20	20	20	20	20
Phenols, cresols and xylols	10			10		
Phosgene	1			1		
Tetrachloro ethane				5		
Trimethylamine	2					
Vinyl chloride				5		
VOC Total Class A	20	20	20	20	20	20
VOC Total Class B	80	80	80	80	80	80

#### Notes

1. The reference conditions applicable to the above levels are: temperature 273 K (0 °C), pressure 101.3 kPa (1 atmosphere), no correction for water vapour or oxygen.
2. Where possible, releases of VOCs should be individually identified. The VOC concentration levels apply where the following total mass release rates are exceeded:
  - Total Class A - 100 g hr<sup>-1</sup>;
  - Total Class B - 5 t yr<sup>-1</sup> or 2 kg hr<sup>-1</sup>, whichever is the lower (expressed as toluene).

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.

3. 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.
4. All releases should be essentially colourless, free from persistent trailing mist or fume and free from droplets.
5. Releases from the processes should not give rise to an offensive odour noticeable outside the site where the process is carried on.

In relation to waste water and BAT the process of analysis of the scope and nature of the problem is more important than the detailed discharge limits that are eventually achieved, which have anyway to be assessed in relation to the receiving waters before authorisation. Water use minimisation and waste water characterisation are, therefore, important components of BAT. Unless the effluent produced by a process is disposed of separately (e.g. by incineration) because of its toxicity, persistence or aesthetic properties it is concluded that it will usually be BAT for effluents to receive at least biological treatment before being discharged to surface waters. This can be done either at the company's own biological treatment plant or, if discharged to sewer, in the water company's sewage treatment plant. To ensure the operation of the biological treatment plant is not affected by the effluent discharged from the process the effluent may need to receive special treatment to reduce toxicity or the concentration of the non-biodegradable fraction in waste water before it is discharged to the biological treatment plant. Special treatment may also be required to recover solvents before discharge to the biological treatment plant to limit the release to air of the VOCs during biological treatment.

For processes like pesticide and pharmaceutical manufacture a measure of the loss to water of active ingredient would be appropriate and deviations from a guide value of 0.1-1 mg kg<sup>-1</sup> of product should be justified by the process owner. It should be noted, however, that processes with inherently low product yields may have difficulty meeting this value.

In the absence of other guidance, limits set in Directives can be used as the basis for deriving benchmark values. These limits were not derived for industrial waste water treatment plants and therefore considerable care should be exercised in their use. These proposed benchmark release levels are outlined in Table 10.8 below. The diversity of the sector needs to be borne in mind and the expectation is that deviations from these values are likely to occur. The reasons for any such deviations should be clearly identified by process owners and therefore be available for scrutiny and challenge if necessary.

**Table 10.8 Proposed benchmark release levels for water**

Substance	Initial guide	Comment/Source
COD	125 mg l <sup>-1</sup> daily average	91/271/EEC
BOD	25 mg l <sup>-1</sup> daily average	91/271/EEC
Suspended solids	35 mg l <sup>-1</sup> daily average	91/271/EEC
Total nitrogen	15 mg l <sup>-1</sup> daily average	91/271/EEC
Total phosphorus	2 mg l <sup>-1</sup> daily average	91/271/EEC
mercury	0.05 mg l <sup>-1</sup>	84/156/EEC
cadmium	0.2 mg l <sup>-1</sup>	85/513/EEC

### 10.3.6 Releases to land

No benchmark values are proposed for releases to land. Instead the emphasis should be prevention and minimisation at source.

## 11. BPEO, SUSTAINABLE DEVELOPMENT AND OTHER CONSIDERATIONS

The Environment Agency has a number of duties imposed on it that are relevant to the authorisation of processes under IPC. The three most important ones are probably:

- the duty to promote sustainable development;
- the necessity to ensure that the best practicable environmental option (BPEO) is chosen for process authorisation when releases are likely to affect more than one medium;
- the duty to have regard to the costs and benefits of their actions.

In relation to IPC the latter point can be considered to be part of the NEEC element of BATNEEC as is indicated in the Ministerial guidance given to the Agency and published in November 1996. As such it is discussed in more detail in Appendix III. But the other two duties are more problematic to interpret in practical terms. This section attempts to produce some guidance.

### 11.1 Sustainable development

Despite the millions of words that must have been written about sustainable development it is very difficult to provide specific guidance on what should be done in a specific instance in order to promote it. The Ministerial guidance given to the Agency states that "The concept of BPEO is central to IPC. The most sustainable form of development is that which achieves the optimum distribution of any pollutants remaining to be released to the environment after they have been minimised under BATNEEC to the three media of air, water and land, according to the ability of those media to accept such pollutants, without, for example, exceeding critical loads." However, it then goes on to say that "Ministers expect the Agency to continue to apply the concepts of BATNEEC and BPEO through IPC authorisations in such a way as to ensure that its IPC functions respect the principles of sustainable development." This implies that more needs to be done than simply applying BATNEEC and BPEO under IPC in order to promote sustainable development.

Issues like resource use and post site usage should thus become part of the decision making process. The problem is that currently these fall outside the span of regulation and therefore of authorisation. Many of these aspects will become part of an IPPC authorisation but until these are brought under the regulations the Agency's role is probably limited to encouraging process owners to consider these issues.

The main initial areas where sustainable development could be promoted are:

- incorporating environmental protection considerations into process and product research and development;

- identifying, purchasing and installing equipment with a minimum impact on the environment, for example pumps and valves that minimise fugitive losses;
- lower utility, for example electricity and water, and raw material use, for example via solvent recovery and reuse, although the wider impact on the environment of such activities should not be overlooked;
- encouraging a wider perspective of process operation, for example up and down stream implications such as transport and packaging;
- taking a longer term view of the process and site and the synergies that can be obtained by sharing heat, power, water and raw materials via recycle/reuse circuits;
- consideration of the wider implications of using abatement techniques, for example their consumption of utilities and raw materials;
- considering social and economic implications of process operation some of these aspects may involve interaction with other regulators e.g. planning authorities and organisations such as local community groups or conservation groups.

It is intended that this study's emphasis on the use of management and process techniques should contribute significantly to the integration of sustainability into this sector.

## 11.2 BPEO under IPC

Under the existing regulations BPEO considerations in authorisations relate to environmental effects arising from process releases. So the concept of BPEO used more generally e.g. that introduced by the Royal Commission for Environmental Pollution is a much broader concept than IPC BPEO. The principles to be used and the approach that could be used to identify BPEO have been published recently and this can be referred to for further general guidance and information.

BPEO considerations in essence boil down to trying to answer questions like: Is it less harmful overall to release chemical X to air or to water? The problems come because the damage caused by X is difficult to predict and often affects different organisms in the different media but also, in transferring X from one medium to another, resources are used and other wastes are created. In practice there are also many other chemicals involved in the waste streams.

In the organic chemicals sector many process options are eliminated in the early stages of process design which is where consideration of BPEO should start. By the time a process design has advanced to the stage where an authorisation is being considered or prepared in most cases few alternative options remain which are all BATNEEC.

It follows that in practice, for this sector, a formal BPEO assessment at the authorisation application stage may not be particularly helpful. Of more use would probably be an earlier, lower intensity screening of the environmental implications of all options considered, with an audit trail maintained of decision making.



## **12. SECTOR SPECIFIC ISSUES**

This section addresses a number of issues that may be of particular interest to inspectors when dealing with the sectors covered by this study. The issues addressed have been selected in consultation with the Environment Agency and are not intended to be exhaustive in their coverage.

The issues covered are:

1. Releases of volatile organic compounds (VOCs).
2. Endocrine disruptors.
3. Ozone depleting substances.
4. Direct toxicity assessment (DTA).
5. Potential dioxin formation.

Each of these issues is discussed in more detail below.

### **12.1 Volatile organic compounds (VOCs)**

Volatile organic compounds (VOCs) are important precursors, together with nitrogen oxides ( $\text{NO}_x$ ), in the formation of low level ozone. Photochemical reactions between VOCs and  $\text{NO}_x$  take place over a long period of time, resulting in elevated concentrations of low-level ozone long distances away from the original source of the contaminants. Short term effects of elevated ozone levels include changes in pulmonary function, increased airway responsiveness to broncho-constrictors and airway inflammation. The current UK air quality standard for low level ozone is 50 ppb, expressed as a running eight hour mean.

#### **12.1.1 Government Policy on VOC emissions from industry**

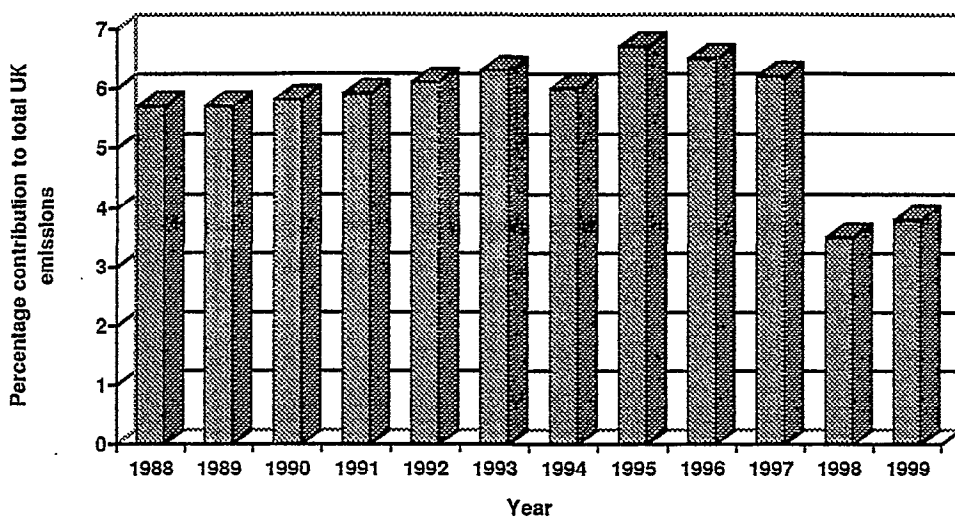
Government estimates indicate that industry contributed 1195 kt (53%) of the 2257 kt of VOCs emitted in the UK in 1995. The Environment Agency and SEPA are required to take account of the UK Air Strategy (DoE 1997) when using their powers vested under the Environmental Protection Act 1990 to control pollution from prescribed processes. However, this must fit into the general concepts of BPEO and BATNEEC.

The Government has calculated that reductions of VOC and  $\text{NO}_x$  emissions in the range 50-70% relative to 1997 levels, while they would not completely remove exceedences of either the recommended EPAQS level of the EU Ozone Directive information threshold, would significantly reduce the extent to which they are exceeded.

The complex nature of the atmospheric chemistry for ozone formation from the presence of VOCs and  $\text{NO}_x$  means that a reduction in VOC or  $\text{NO}_x$  emissions from UK sources may not lead to a direct reduction in ozone concentrations in the UK. Unilateral action taken by the UK

is likely to have a significant effect of the extreme peak ozone concentrations in the UK, but ozone episodes will still occur if UK emissions were eliminated. Therefore any strategy for reductions in VOC emissions must be developed in the context of measures taken at an EU and international level (see Section 1.3).

The contribution to the UK's total VOC emissions from the Chemical Industry, together with forecast levels to 1999, are displayed in Figure 12.1. No data for the UK could be found on the contribution each sector within the chemical industry makes to these emissions.



**Figure 12.1 Emissions of VOCs in the UK from the Chemical Industry, 1988-1999 (excluding forests) (DoE 1997)**

### 12.1.2 Categorisation of VOCs

VOCs have a variety of direct and indirect impacts on man and the environment, the main concerns being:

- harmful effects on human health and on natural ecosystems through toxicity, carcinogenicity and other adverse physiological effects;
- damage to materials;
- tropospheric photochemical oxidant formation;
- stratospheric ozone depletion;
- global climate change; and
- odour.

Her Majesty's Inspectorate of Pollution (HMIP), now incorporated into the Environment Agency, contracted AEA Technology to prioritise VOCs in terms of the above effects. A total

of 377 chemicals were prioritised using the procedure displayed in Figure 12.2. By following this decision tree, approximately 50 VOCs have been classified as "high priority". These are listed in Table 12.1.

**Table 12.1 Proposed "High" Category VOCs (HMIP 1995b)**

Acrylamide	Dichlorvos	2-Nitropropane
Acrylonitrile	Dieldrin	Phenol
Azinphos-methyl	Diethyl sulphate	Phorate
Benzene	Dimethyl disulphide	Phosgene
Benzene-1,2,4-tricarboxylic acid 1,2-anhydride	Dimethyl sulphate	Polychlorinated biphenyls
Benzo (a) anthracene	Dinoseb	Polychlorinated dibenzo-p-dioxin - all congeners
Benzo (b) fluoranthene	Endosulfan	Polychlorinated dibenzofuran - all congeners
Benzo (k) fluoranthene	Endrin	2-Propen-1-ol (allyl alcohol)
Benzo (j) fluoranthene	2-Ethoxyethanol	Propylene oxide
Benzo (a) pyrene	2-Ethoxyethyl acetate	Pyrene
Butadiene	Ethylene oxide	1,1,2,2-tetrachloroethane
Carbon disulphide	Hexachlorobenzene	p-Toluene diamine
1-Chloro-2,3-epoxypropane (epichlorohydrin)	Isophorone di-iso cyanate	Toluene-3,4-diamine
Chloroethene	Maleic anhydride	Toluene-2,6-diamine
Cyanamide	4,4'-methylenebis [2- chloroaniline]	Toluene-1,3-diisocyanate
Cyanamide (ACGIH, OSHA)	4,4'-methylenediphenyl diisocyanate	Toluene-2,4-diisocyanate
Dibenzo (a,h) anthracene	Methyl isocyanate	Toluene-2,6-diisocyanate
1,2-Dichloroethane	Nitrobenzene	Trimellitic anhydride

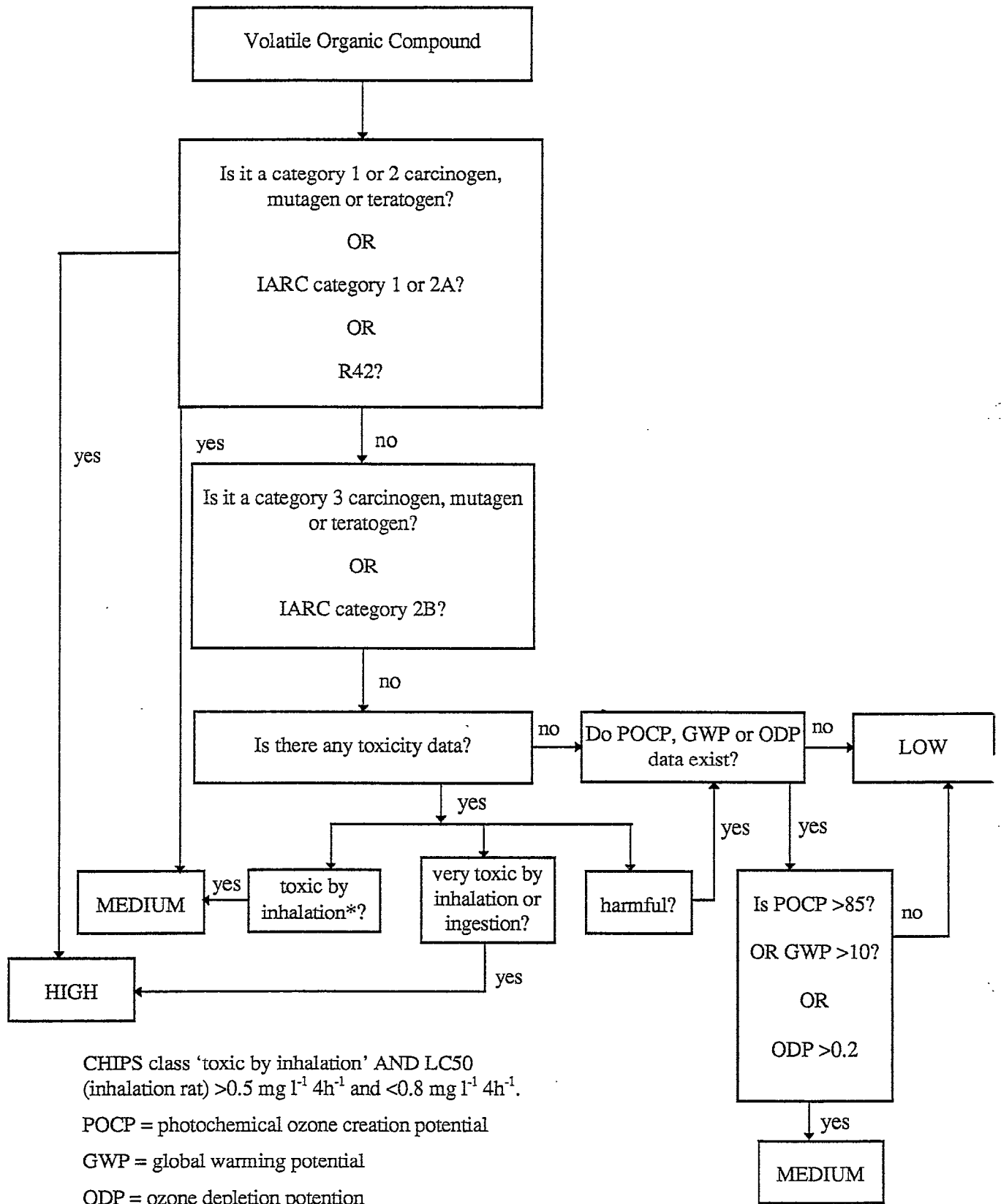


Figure 12.2 The categorisation decision tree for VOCs (HMIP 1995b)

## 12.2 Endocrine disrupting chemicals

A number of well publicised media stories and concerns has brought this issue into the public arena and the Environment Agency has recently published a Consultation Report on the subject ("Endocrine disrupting substances in the environment: what should be done").

Certain chemical substances have the ability to disrupt the normal operation of the endocrine system of animals. The endocrine system regulates many physiological processes in animals usually by the production and movement around the body of hormones. The most widely reported endocrine disruption concerns the control of the sexual functions of animals, particularly those of fish.

Male fish downstream of some sewage discharges in the UK are more likely to show female characteristics than male fish from upstream or control areas. The hormones associated with the control of female sexual functioning are called oestrogens, androgens control the male sexual functioning. The agents causing the increase in female characteristics have not yet been identified but the terms hormone-disrupting, anti-androgenic and oestrogenic chemicals have been used together with the term endocrine disruption in describing the phenomenon. In practice all these terms are more or less equivalent, in that the normal sexual development of the fish, in this case, has been disturbed by chemicals apparently present in the sewage discharge.

Similar effects have been reported in dog whelks in coasts and estuaries in the UK associated with exposure to tributyl tin anti-fouling chemicals and in the USA reports of effects on alligators and terns have been attributed to organochlorine pesticides.

The Agency has proposed a priority list of substances and categories of substance for which endocrine disrupting characteristics have been reported. This list is provided in Table 12.2 below.

**Table 12.2 Agency's priority list of endocrine disrupting chemicals**

Substance category	Substances
Organochlorine pesticide	DDT, Drins, Lindane, Endosulfan
Polychlorinated chemical	PCBs, Polychloro dioxins and furans
Other pesticides	Atrazine, Dichlorvos, Simazine, Tributyl tin compounds Trifluralin, Demeton-S methyl, Dirnethoate, Linuron, Permethrin, Diazinon, Clorfenvinphos
Alkylphenols and ethoxylates	Nonylphenol, Nonylphenol ethoxylate, Octylphenol, Octylphenol ethoxylate
Steroids	Ethinyl oestradiol, 17- $\beta$ oestradiol, Oestrone
Other synthetic chemicals	Bisphenol-A, Phthalates

Many of the chemicals listed above are already “priority” substances for control. The discovery that these chemicals also possess the potential to disrupt the endocrine systems of animals places an additional emphasis on the need to explore options that minimise the release of these chemicals from processes.

### 12.3 Ozone depleting substances

The Vienna Convention for the Protection of the Ozone Layer was adopted under the auspices of the UNECE in 1985 and provides a framework for the protection of the ozone layer. The Montreal Protocol, adopted in 1987, is the practical mechanism for implementing the Convention. The Protocol identifies the main ozone depleting substances and the controls, mainly based on phased reductions in their production and use, to be applied to them. EU Member States have agreed to accelerate some of the phased timetable. This timetable, as it applies to Member States, is summarised in Table 12.3 below:

**Table 12.3 Phased timetable for the reduction in use of ozone depleting substances, as it applies to EU Member States**

Substance	Deadline
CFCs	85% reduction by 1/94 100% by 1/95
Halons	100% by 1/94
Carbon tetrachloride	85% by 1/94 100% by 1/95
HCFCs	stabilise at 1991 levels by 1996 35% reduction by 2004 90% by 1/2015 99.5% by 1/2030
Methyl bromide	stabilise at 1991 levels by 1/95
HBFCs	progressive elimination by 1/96
1,1,1 trichloroethane	50% 1/94 100% 1/96

### 12.4 Direct toxicity assessment (DTA)

Many of the effluents produced by this sector are complex and thus may be particularly amenable to control based on direct toxicity assessment (DTA). The Agency, in collaboration with industry and SNIFFER, is currently supporting a demonstration project to assess the feasibility of using DTA as a regulatory tool. This demonstration project will involve the

application of DTA protocol at four locations in the UK over the next 12-18 months (Environment Agency 1998).

The protocol consists of seven stages, which may be summarised as:

1. Prioritisation of location.
2. Selection of discharges.
3. Characterisation of toxicity and assessment of dilution and dispersion of discharges.
4. Assessment of need to reduce toxicity of discharges.
5. Discharge improvement plans (Toxicity reduction evaluation).
6. Discharge improvement plans (Toxicity reduction).
7. Post improvement plan appraisal.

The role of DTA in the regulation of the sector will become clearer once this demonstration project has been completed.

## 12.5 Dioxins

The issues and problems associated with chlorinated dioxins and furans are well known and the well documented aspects of this group of chemicals relating to properties, nomenclature, sources and control will not be repeated here.

Two main sources of chlorinated dioxins and furans have been identified. One is as a by-product of chemical processes usually involving chlorinated phenols. The other results from combustion of a wide variety of organic material under a wide variety of conditions. Yields of dioxins and furans from combustion processes are often very low but, because of concerns about their toxicity and persistence, still of significance. The physico-chemical processes leading to their production during combustion are still incompletely understood but do appear to be ubiquitous with traces of the compounds being found from a very wide variety of combustion processes.

Of more direct relevance to the organic chemical sector is the formation of dioxins and furans in chemical processes. Here the reactions involved are better understood and certainly historically the reactions have yielded higher concentrations of dioxins and furans than combustion processes. Simple heating of the alkali metal salts of chlorophenols can produce 10-80% yields of chlorinated dioxins and furans. The role of the alkali metal in promoting the reaction does appear to be important and other metals can play a similar role. All processes involving chlorophenols therefore deserve special consideration from the point of view of dioxin and furan production - as has been demonstrated by the accident at Seveso. It is notable that the Coalite plant at Bolsover, which was a notable source of dioxin and furan pollution in the UK, was involved in chlorophenol production.

Based on the similarities between the reactions and behaviour of chlorine and bromine chemicals, processes involving bromophenols should also give particular consideration to the potential for brominated dioxin and furan production.

Information on dioxin and furan residues is summarised in the following sections but the general guidance relating to dioxins and furans relating to the organic chemical industry is:

- pay particular attention to any process involving chloro (or bromo) phenols especially those using metal salts or metal catalysts;
- chemical processes involving heating chlorinated aromatics should be considered for their potential dioxin and furan production.

### 12.5.1 Air

Of the processes studied in its review of emissions of PCDD/F to air, HMIP (1995c) concluded that the following processes were unlikely to give rise to significant dioxin emissions:

- acid processes;
- *inorganic chemical processes*;
- the production of chemical fertilisers;
- pharmaceutical production; and
- the storage of chemicals in bulk.

No data could be found on the emissions of PCDD/F from processes involving halogens, apart from the manufacture of vinyl chloride monomer (VCM). Based on data from VCM manufacture it was estimated that 0.02 g TEQ are produced per year from halogenated processes.

On the production of pesticides HMIP (1995) concluded that the potential for release of pesticides is very low, and based on very limited data calculated that 0.1 - 0.3 g TEQ are emitted per year to air.

### 12.5.2 Water and land

The results of studies on the concentrations of dioxins in freshwater biota and sediments have indicated that the main source of dioxins in water may be atmospheric deposition (McDonagh 1997). However, minor sources have been identified in a recent review of dioxin emissions to water and land carried out by the Environment Agency (1997g).

#### **Chlorinated aliphatics (other than PVC, perchloroethylene, trichloroethylene)**

The Environment Agency reported that no data are available on the PCDD/F emitted to water and land from these processes, although the use of direct chlorination rather than oxychlorination is expected to result in the formation of significantly lower levels. Releases to water are expected to be lower than for the production of PVC, perchloroethylene and trichloroethylene.



## Pesticide Production

The majority of wastes arising from the production of pesticides are likely to be designated as "special waste" and their disposal will therefore be tightly controlled. The production of pesticides that involve chlorination processes or chlorinated phenols in their production are most likely to lead to the formation of PCDD/F. However, there are few data available on the concentrations of dioxins in the residues from pesticide production. Moreover, as the process conditions and ingredients vary from one product to another, the levels of PCDD/F will vary accordingly.

In 1997, the Environment Agency could find concentration data for PCDD/F only in pyrolysed hexachlorocyclohexane (HCH) residues and trichlorobenzene (TCB) stillbottoms equating to a concentration of 67.4 mg TEQ kg<sup>-1</sup>. These data were deemed to be indicative of the most contaminated waste. PCDD/F was also found in pyrolysed HCH residues up to a concentration of 296 µg TEQ kg<sup>-1</sup>. No data were found on the concentration of PCDD/F in releases to water.

Based on the data above and estimated production levels, the Environment Agency (1997) estimates that releases of PCDD/F to land from the production of pesticides could be of the order of 8.9 - 2000 g TEQ year<sup>-1</sup>. The Agency also estimates that releases to water could be 0.0089 - 2.0 g TEQ y<sup>-1</sup>, based on releases to water being 0.1% of those to land.

## Pharmaceutical production

The Environment Agency could find no data on the formation of PCDD/F in pharmaceutical production.

## Sewage sludge

Polychlorinated dibenzo-p-dioxins and dibenzofurans have been found to be present in sewage sludge at concentrations of 30-100 ng TEQ kg<sup>-1</sup> dry weight even in the absence of industrial sources. The levels of PCDD/F from one sewage treatment plant in Germany have been investigated to determine the contributions of different sources. From this study the authors observed that approximately 4% of the dioxin was due to run-off from roofs and streets and up to 25% from domestic wastewater.

By measuring the concentration of dioxins in laundry wastewater, the authors conclude that this is a major source of dioxins in household wastewater (Horstmann *et al*, 1993). However, it is likely that the original source of this dioxin contamination is from the use of pentachlorophenol in the textile industry (Environment Canada 1996). There is still some controversy surrounding the potential formation of PCDD/Fs in sewage treatment works.

In a further study sludge samples from two pharmaceutical plants in Sweden, in Södertälje and Uppsala, were found to contain low PCDD/F levels with annual emissions of  $2 \times 10^{-4}$  and  $4 \times 10^{-7}$  g NTEQ<sup>1</sup> respectively (Lexén *et al* 1993).

<sup>1</sup> NTEQ = Nordic Toxic Equivalent

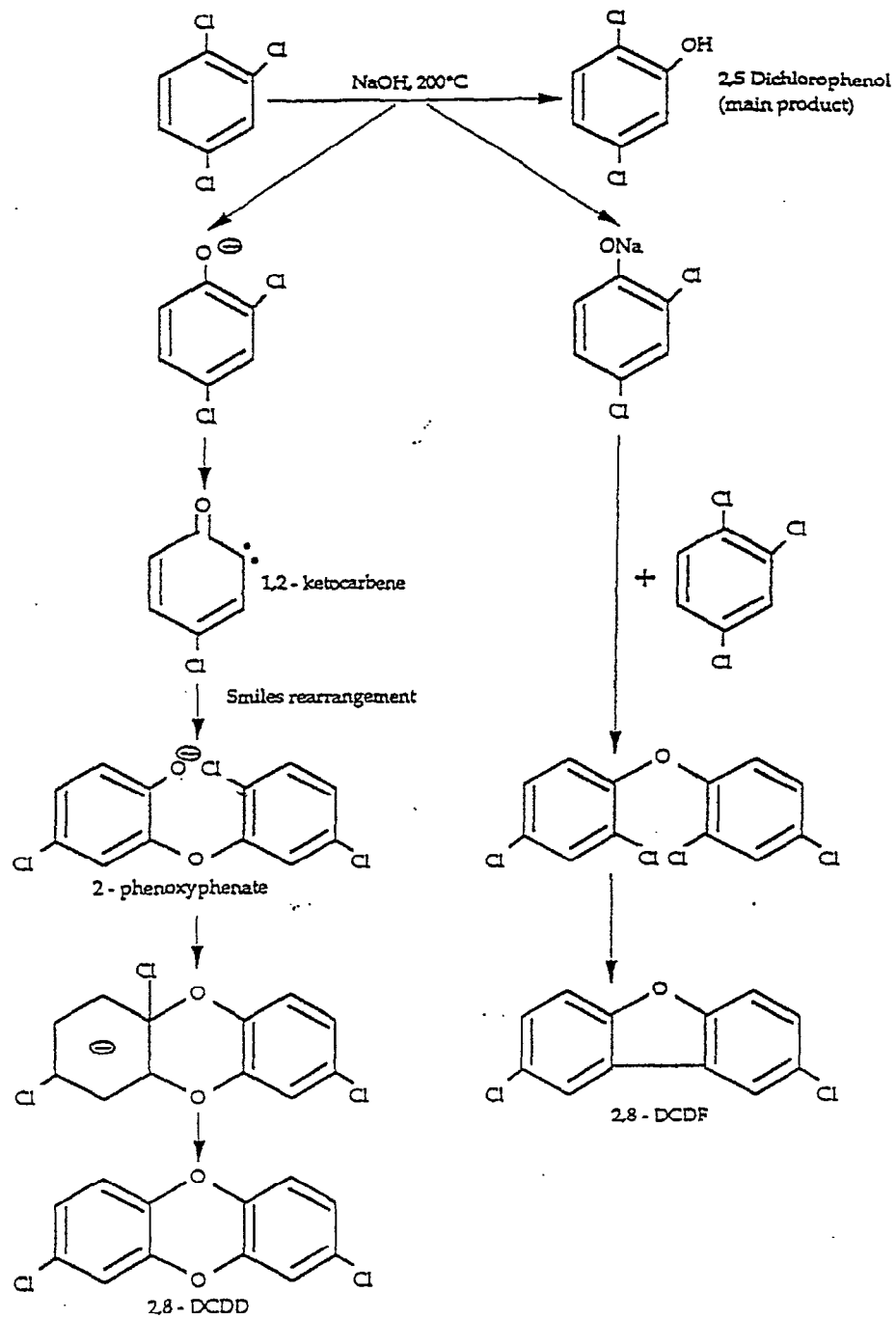


Figure 12.3 Routes for the formation of dioxins

## 13. CONCLUSIONS

Recent developments in processes and practices relating to best available techniques (BAT) have been reviewed for the fine and speciality organic chemical sector (the sector). This sector covers the following types of production process:

- organo-metallics;
- sulphonation and nitration;
- halogenation;
- pesticides;
- pharmaceuticals.

The results of this review have been used to underpin the preparation of an updated draft IPC Guidance Note for the sector. The main findings and conclusions of the review are discussed below.

### 13.1 The Sector

The sector considered in this study encompasses approximately 750 processes in England and Wales. It is an important sector comprising about one third of all those currently authorised by the Environment Agency under the IPC regime. The sector is characterised by a diverse range of raw materials, reaction chemistries, production processes and products. This size and diversity makes it particularly difficult to be specific about BAT and associated benchmark release levels for the sector because direct inter process comparisons are rarely possible and there are usually special circumstances applying to individual processes.

Notwithstanding these limitations, a structure has been developed that allows commonality to be identified within the sector. This structure is based on the recognition that most processes will utilise one or more of the following five unit processes:

- storage and raw material handling;
- plant systems and equipment;
- reaction;
- separation;
- purification and/or final product preparation.

The environmental releases and associated techniques to prevent, minimise and render them harmless are generally fundamentally the same for these unit processes whatever the process being considered. There are, however, issues that are specific to each type of process and these will often require the application of specialist techniques that may not be appropriate for other processes.

## 13.2 Techniques

A wide range of techniques are available for preventing, minimising and rendering harmless releases from this sector. To provide a structure within which to discuss them, three types of technique have been identified. These are:

- management techniques;
- process techniques;
- abatement techniques.

The diversity of the sector and the need to promote pollution prevention/minimisation at source means that particular emphasis needs to be given to the utilisation of management and process techniques. It is a major conclusion of this study that further improvements in the environmental performance of this, and other, IPC sectors is largely dependent on the successful implementation of these techniques.

### 13.2.1 Management techniques

Management techniques relate to the systems and procedures that the operator utilises to prevent, minimise and render harmless releases. Although there is no unique way of managing a process, this study suggests that a significantly higher priority needs to be placed on the inspector understanding the operator's approach to managing the process.

Some of the main management areas that an inspector could expect an operator to consider have been identified, together with examples of some of the techniques that could be used. These areas include:

- senior management commitment - without this, no technique, however well designed and implemented, will be successful in the long term. Surveys and experience suggest that environmental protection is assigned a relatively high profile in the sector. Many companies have translated this into a senior management commitment, for example via published policies and the implementation of accredited management systems. However, a significant minority has yet to make this move and even for those that have, there is the potential for the commitment not to be translated into practical measures. Inspectors should therefore be looking not just for the indicators of commitment but practical examples of successful implementation, some of which are discussed below;
- organization and responsibility - a clear structure for managing environmental issues should be in place. This should include the integration of process with wider site and company environmental management. At many multi-process sites a management committee is the key tool for asserting day-to-day control and overseeing planning. Inspectors should ensure that all aspects of ensuring compliance with the authorisation are discussed on a regular basis by such a committee with a minuted record of decision making retained. Whilst clear definition of the operator's interface with the Agency is required, this should not be used as an excuse to preclude the involvement of all staff in ensuring that the authorisation is complied with;

- maintenance - is an important way of ensuring that process and abatement techniques are operating optimally and that breakdown, and associated release, is minimised. A proactive, rather than reactive, approach to maintenance would be expected in most cases. For example, a leak detection and repair (LDAR) programme can be used to minimise fugitive losses, albeit one conducted at a lower intensity than may be expected in the petrochemical sector;
- process control - ensures that the operator has full control over the process at all times, that yields are maximised and releases minimised. It is particularly important that all information relating to process performance is collected for a clearly defined purpose, that it is assessed on a regular basis, trends are identified and that robust and easily accessible records are maintained. The use of indicators to relate environmental performance to production or resource use may offer particular advantages. However, the difficulties of utilising them in a sector characterised by batch operations should not be underestimated;
- waste minimisation - regular audits of raw material and utility use and waste arisings should be used to identify opportunities for improvement. Extensive guidance has now been issued on this topic and it would be expected that any operator that has not implemented a programme has a sound reason for not doing so. Waste minimisation can also be an important mechanism for involving all staff in preventing and reducing releases and it could be expected that recognition is given to those who identify significant improvements;
- process and product design - the best way of preventing and minimising releases is to consider them during the design of the process and/or product. Those involved should be encouraged to consider critically the environmental implications of the process and give adequate consideration to alternative process options at all stages in the design procedure. Operators should be encouraged to involve inspectors at as early a stage as possible in the design procedure and to maintain a robust audit trail of decision making;
- staff training and awareness - all staff should be made aware of their contribution to preventing, minimising and rendering harmless releases. This can be augmented by ensuring that environmental performance is included in the appraisal of key staff. Staff should also be given training where relevant, with records being maintained. A number of process operators drew attention to the usefulness of previous NRA videos on pollution prevention. The Agency may wish to consider whether it would be advisable to provide an update covering all aspects of IPC, not just protection of the aquatic environment;
- incidents - operators should have procedures in place to respond to incidents, report them internally and, where relevant, to the Agency and ensure that lessons are learnt from them. Emergency procedures should be tested under all credible situations, not just during core working hours. Individuals with responsibility for the environment should be regularly involved in the incident reporting and investigation systems. The Agency may also consider it desirable to provide greater guidance to operators on the type of incident that should be reported to inspectors;

- finance and accounting - wherever possible the true costs of releases and their control should be identified and attributed to the process. This helps prioritise the main sources of releases and can also provide process operators with an incentive to reduce waste arisings. Consideration should also be given to the environmental implications of purchasing decisions. For example, ensuring that contractors fully understand the environmental implications of their activities and that raw materials specifications minimise the presence of impurities that can contribute to waste arisings.

International environmental management standards (ISO 14001 and EMAS) have been developed and where these have been implemented they may offer a useful template to assess an operator's approach to utilising management techniques. Although implementation of these standards is not obligatory it may be expected that an operator would have a management system in place for ensuring compliance with the authorisation. The form that it takes will vary from operator to operator, for example some may choose to integrate it with health and safety systems, but an Inspector could reasonably expect it to cover the points outlined above in a systematic and auditable manner that has been communicated to all staff.

### 13.2.2 Process techniques

Process techniques are the, usually physical, techniques that an operator can use to prevent and minimise releases during process operations. They have been discussed in terms of the five unit processes outlined above.

As with management techniques there are multiplicity of process techniques and it is difficult to be specific about which should be used. Inspectors would, however, want to ensure that operators had considered the releases that may arise under both routine and non-routine conditions from their unit processes. Such a consideration may include:

- the identification, quantification and assessment of the impact of all potential releases;
- the prioritisation of releases that merit control;
- the implementation of process techniques to control these releases.

The main process techniques that can be applied to deal with these releases are:

- storage and handling of raw materials, products and wastes. The sector is characterised by the storage and handling of relatively small amounts of a wide range of substances. Storage and handling arrangements therefore need to be flexible but equally attention should be paid to how, in particular, storage is managed in an attempt to minimise inventories of materials that are held. The main physical techniques that need to be applied relate to the retention of spills and/or fire fighting water, with particular attention being paid to the isolation of drainage systems;
- plant systems and equipment (e.g pumps, compressors, relief valves, valves etc). The main consideration is the minimisation of fugitive losses. Whilst these are not on the scale of fugitive emissions, for example, from a large petrochemical process, a number of relatively simple solutions can be adopted to minimise losses. Consideration also

needs to be given to utility use, in particular energy and water, which will become significant issues with the implementation of the IPPC Directive;

- reaction. For new plants attention needs to be paid to designing reactors to minimise releases, in particular by reducing fugitive losses, ensuring that condensers maximise the return of reagents to the reactor and that waste arisings from washdown are minimised. For existing reactors, such changes can be harder to achieve but physical and procedural changes can still be used to improve performance;
- separation. The main issues are enhancing separation to maximise product recovery and managing the addition of materials that may be added to the reaction mix to enhance separation but which may themselves result in releases; and
- purification. Consideration needs to be given to the potential for recovering and reusing purge streams but by and large reducing releases during purification, and to a lesser extent separation, is usually dependent on upstream modifications. For example, by reducing levels of impurity in raw materials, modifying reaction conditions, improving catalyst recovery and reducing the ingress of contaminants such as air during other process stages.

### 13.2.3 Abatement techniques

Abatement techniques are the end-of-pipe techniques that can be applied to control pollution once it has been formed. Although abatement techniques will continue to play an important role in IPC, their use should only be considered once all viable management and process techniques have been implemented. They have been discussed in terms of:

- air abatement techniques;
- waste water abatement techniques;
- land abatement techniques.

#### Air abatement techniques

The release of volatile organic compounds (VOCs) is by far the most significant factor when considering the abatement of releases to air from this sector. Other pollutants (acid gases, particulates etc) are released but existing Agency guidance on their abatement is also generally applicable to this sector.

There are five basic techniques for abating releases of VOCs and given the diversity of the sector all will be BAT under particular circumstances. The main differentiating factor between them is that three are recovery techniques, whilst the other two are destructive.

The three recovery techniques (adsorption, absorption and condensation) all offer opportunities for subsequent recycle or reuse, although if this is not feasible, further treatment and/or disposal of the recovered VOC will be required. The two destructive techniques (biological and thermal oxidation, respectively) do not allow recovery but given the complexity of the gas streams generated in this sector, recovery is often not a viable option.

A number of recent developments in air abatement techniques may have particular implications for this sector. These are:

- catalytic oxidation is now a more robust technique than it was previously, less susceptible to problems associated with the poisoning of catalyst beds. However, there are likely to be a number of situations (e.g fluctuations in flow, concentration and the VOCs present) characteristic of this sector where it is insufficiently flexible to merit use;
- biological oxidation has developed rapidly as a control technique, although its use is still restricted to fairly constant flows, containing VOCs that biodegrade relatively quickly. In addition, certain substances and gas stream characteristics (high temperatures, acids etc) that are prevalent in this sector may harm the biological community involved in the biodegradation;
- cryogenics allow much lower condensation temperatures to be achieved, broadening the range of VOCs that the technique can be applied to whilst improving removal efficiencies. However, the high operating costs of such systems means that their use may be hard to justify unless a process utilises liquid nitrogen for other purposes;
- flameless thermal oxidisers appear to have a number of advantages compared to other thermal techniques. Secondary fuel requirements and the potential for the formation of secondary pollutants is much less than for thermal oxidation. In addition, they are more robust than catalytic oxidisers. They may be particularly amenable for dealing with the large fluctuations in flow rate and concentration that are characteristic of this batch based sector.

### **Waste water techniques**

The sector gives rise to a diverse range of waste waters. This means that it is particularly important that waste water issues associated with a process are fully characterised before any decision is taken on which abatement technique(s) to apply. This enables opportunities for process modification to be identified to prevent releases at source. It also allows streams to be blended or segregated to obtain the optimum characteristics for subsequent treatment.

Water use is intrinsically linked to waste water abatement in this sector and a high priority should be assigned to considering how water use can be minimised without adversely affecting subsequent treatment.

Four types of waste water abatement technique have been identified. These are:

- special treatment, which is applied to waste streams that may be resistant or inhibitory to central treatment, odorous or offer opportunities for recovering solvents etc;
- pre-treatment, is used to prepare waste streams for a later, usually, more complex, abatement stage, or, in certain cases, as the main treatment prior to discharge to sewer;



- central treatment, consists of biological treatment, to remove biodegradable compounds, and/or chemical coagulation to remove metals and other solids;
- polishing treatment, is usually applied as the last treatment stage before discharge and is usually targeted at specific pollutants that have proved resistant to earlier treatment.

Many processes will require a combination of these types of treatment to be applied. Although the techniques utilised will always be a process specific consideration it may be expected that many processes will require a biological technique to be applied, whether it be on-site or off-site in a sewage treatment works.

Greater emphasis should be paid to identifying opportunities for utilising special treatment techniques on individual, segregated waste streams.

### **Land abatement techniques**

It is difficult to provide guidance on techniques for preventing, minimising and rendering harmless releases to land. A higher priority, however, needs to be paid to the systems (management techniques) that are utilised to deal with releases to land e.g by implementing a waste minimisation programme.

### **13.3 Innovation in techniques**

Innovations will continue to be made in all of the techniques discussed above but no one development has been identified that is likely to have a significant impact on its own.

### **13.4 Benchmark release levels**

The derivation of benchmark release levels for this sector is particularly difficult. The main problems are that:

- benchmark release levels are generally more difficult to achieve with the intermittent releases that are characteristic of the batch production processes prevalent in this sector rather than from continuous releases;
- levels quoted in the literature and by manufacturers are usually based on a simple gas stream containing a single VOC. In practice, gas streams in this sector are likely to contain many VOCs, moisture, particulates and acid gases, all of which may prevent the optimum release level being achieved;
- there are a wide range of reaction chemistries, raw materials, products and releases in the sector, with the result that what is achievable by one process may not be achievable by another;
- the traditional source of information on release levels, standards or guidelines set by other countries/international organizations, may not be adequate for a sector as

complex as this. These standards/guidelines are usually applied as a part of a wider suite of conditions and their use in isolation may be inappropriate.

Notwithstanding these limitations, benchmark release levels remain an important tool for inspectors and considerable attention has been given to how existing levels may be tightened in line with changes in BAT as well as new levels introduced.

An extensive range of benchmark release levels has been introduced for releases to air and little scope for the further tightening of these standards has been identified. The one exception is for SO<sub>x</sub> and NO<sub>x</sub>, where a tightening of the existing standard of 300 mg/m<sup>3</sup> to 200 mg/m<sup>3</sup> is proposed.

New benchmark release levels have been proposed for releases to water for a number of parameters. The basis for proposing these levels is probably not as robust as it is for releases to air and as such they should be applied with care, in particular for COD.

### **13.5 BPEO/Sustainability**

The impending implementation of the IPPC Directive would appear to be particularly relevant to this sector. The sector makes extensive use of utilities such as energy and water and there appears to be considerable scope for reducing this usage.

### **13.6 Sector specific issues**

A number of sector specific issues have been considered that may merit particular attention by Inspectors. The main issue, the control of releases of VOCs, has been discussed in the sections on air and waste water abatement techniques, respectively. There is little evidence to suggest that releases of dioxins are an issue in this sector, although a few, very specific circumstances where they may merit attention have been identified, for example where chlorophenols are being used.

Endocrine disrupting compounds and the related topic of direct toxicity assessment are still at too early a stage in their understanding for definitive conclusions to be reached, although it is likely that they will be issues for this sector in the future.

### **13.7 Economics**

Approximately 370 companies hold IPC authorisations in this sector. Whilst many can be said to be dedicated producers of fine and speciality organic chemicals it is apparent that a significant minority operate predominantly in very different economic markets, for example, food manufacture, aerospace, fuel and construction. In addition, the dedicated producers of fine and speciality organic chemicals tend to sell their products to other companies, who are themselves operating in a very wide range of markets. In this sense the sector, and its economic well being, can be said to be a microcosm of the UK economy as a whole. The heterogeneous nature of the markets that processes in this sector operate within suggests that the Sector Affordability approach may be particularly inappropriate for it.

Whilst recognising the wide range of companies operating in this sector, this study has concentrated on the dedicated producers of fine and speciality organic chemicals. Many of these companies are small and medium enterprises (SMEs) and particular attention needs to be paid to the potential for a disproportionate impact on them when applying BAT.

The market for fine and speciality organic chemicals is global (i.e. the relatively high cost of the products limits the impact of transportation costs). Competitors are likely to be concentrated in the USA, Germany, Switzerland and the Far East. Analysis suggests that investment in the sector is very mobile. At the moment considerably more investment is being made by UK companies overseas than is being made in the UK by foreign companies.

Despite the size of the sector, the construction of new processes is relatively infrequent, with most growth being achieved by mergers and acquisitions. Investment cycles tend to be long, often 25 years or longer. It is therefore important that when new processes are introduced there is a degree of future proofing built into them to anticipate changes in BAT.

A financial analysis of the sector was undertaken and, whilst recognising its diversity, suggests that it is characterised by relatively high returns on capital and assets employed. This reflects the risk of investing in this sector compared to other sectors which may be characterised by lower returns but which have a better guarantee of a long term income flow.

An assessment of the three main options for addressing the need to invest in BAT (passing costs back to suppliers, passing costs through by increased efficiency and absorbing costs via lower profits) suggests that the sector as a whole can probably deal with small to moderate investments.



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# APPENDIX A CATALOGUE OF TECHNIQUES

## MANAGEMENT TECHNIQUES

MT 1	Senior management commitment
MT 2	Organization and responsibility
MT 3	Maintenance
MT 4	Process control
MT 5	Waste minimisation
MT 6	Process and product design
MT 7	Staff awareness and training
MT 8	Finance and accounting
MT 9	Incidents

## PROCESS TECHNIQUES

### Storage Techniques

PST 1	Drainage systems
PST 2	Dry storage
PST 3	Drum storage
PST 4	Tank storage
PST 5	Tanker loading and off-loading

### Equipment Techniques

PSE 1	Ventilation
PSE 2	Leak detection and repair
PSE 3	Over pressure
PSE 4	Vacuum systems
PSE 5	Pumps
PSE 6	Gas compressors
PSE 7	Agitator systems
PSE 8	Valves
PSE 9	Purging
PSE 10	Leakage

### Reactor Techniques

PR 1	Reactor
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## **Separation Techniques**

PS 1	Liquid-vapour separation
PS 2	Liquid-liquid separation
PS 3	Solid-liquid separation

## **Purification Techniques**

PP 1	Liquid purification
PP 2	Solid purification

## **AIR ABATEMENT TECHNIQUES**

### **VOC Techniques**

AV 1	Activated carbon adsorption - General principles
AV 1.1	Fixed bed adsorption
AV 1.2	Fluidised bed adsorption
AV 1.3	Continuous moving bed adsorption
AV 1.4	Canisters
AV 2.1	Coolant/refrigerant condensation
AV 2.2	Cryogenic condensation
AV 3.1	Flares
AV 3.2	Thermal oxidation
AV 3.3	Catalytic oxidation
AV 4	Biological oxidation

### **VOC/Particulate Techniques**

AV 5	Absorption techniques for trace gases
AP 1	Scrubbing techniques for particulates and droplets
AV 5.1/AP 1.1	Packed column scrubbers
AV 5.2/AP 1.2	Plate tower scrubbers
AV 5.3/AP 1.3	Fibrous packing scrubbers
AV 5.4/AP 1.4	Moving (or fluidised) bed scrubbers
AV 5.5/AP 1.5	Spray tower scrubbers

## **Particulate Techniques**

AP 1.6	Venturi scrubbers
AP 1.7	Impingement and entrainment scrubbers
AP 1.8	Rotary scrubbers
AP 1.9	Mist eliminators
AP 2.1	Cyclones
AP 3.1	Electrostatic precipitators
AP 4.1	Fabric or bag filters
AP 4.2	Cartridge filters

## **WASTE WATER TECHNIQUES**

### **Pre-treatment Techniques**

PRT 1	Water insoluble compounds
PRT 2	Solids removal
PRT 3	pH adjustment
PRT 4	Equalisation

### **Special Treatment Techniques**

ST 1	Air stripping
ST 2	Steam stripping
ST 3	Distillation
ST 4	Wet air oxidation
ST 5	Super critical water oxidation
ST 6	Chemical oxidation

### **Central Treatment Techniques**

CT 1	Aerobic biological treatment
CT 2	Anaerobic biological treatment
CT 3	Reed beds
CT 4	Chemical coagulation

### **Polishing Treatment Techniques**

PT 1	Ozone
PT 2	Activated carbon
PT 3	Zeolites
PT 4	Membranes

## MANAGEMENT TECHNIQUES

<b>MT1</b>	<b>Senior management commitment</b>
<b>Pollutants</b>	All
<b>Description</b>	No system for managing a process' impact on the environment can ever be effective without the commitment and support of senior management
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>Senior management can demonstrate its commitment by issuing an environmental policy. This could be based on:</p> <ul style="list-style-type: none"> <li>• an externally accredited management system such as ISO 14001 or Emas</li> <li>• the CIA's Responsible Care Programme;</li> <li>• an in-house system.</li> </ul> <p>When the latter is being used, the inspector will need to assess whether corporate commitment is being translated into practical steps throughout the organization.</p> <p>Commitment can also be demonstrated in terms of non-regulatory reporting and the willingness to fully disclose the company/site/process impacts and how they are to be reduced.</p>
<b>Environmental impacts</b>	All
<b>Costs</b>	<p>To prepare policy - low</p> <p>To implement policy - highly variable depending on commitments</p>



<b>MT2</b>	<b>Organization and responsibility</b>
<b>Pollutants</b>	All
<b>Description</b>	Clearly defined roles and responsibilities are required to ensure that the process' impacts are managed effectively
<b>Availability</b>	Widespread
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• There should be a clearly defined contact point for the IPC authorisation;</li> <li>• There should be clearly defined responsibility for the environment, including complying with the authorisation, throughout the company;</li> <li>• The environment should be a regular agenda item on all process, site and corporate management meetings;</li> <li>• There should be a clear link between those with corporate responsibilities and those with process specific responsibilities;</li> <li>• There are a number of formal environmental management systems (EMSs) such as BS7750, Emas and ISO 14001. Process operators do not have to implement one of these formal systems to ensure that they are managing the environment effectively. However, these systems can provide inspectors with a useful template against which they can assess the effectiveness of the operator's chosen approach.</li> </ul>
<b>Environmental impacts</b>	All
<b>Costs</b>	Variable

<b>MT3</b>	<b>Maintenance</b>
<b>Pollutants</b>	All
<b>Description</b>	Maintenance is an important mechanism for preventing and minimising fugitive emissions, accidents and ensuring that product yields are maximised and associated waste arisings minimised.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• It would normally be expected that maintenance is based on prevention rather than reaction;</li> <li>• Process performance should be monitored to detect areas where performance is deteriorating and maintenance may be required;</li> <li>• Staff should be aware of the contribution they can make by identifying leaks, spills or smells which may be indicators of the need for remedial work;</li> <li>• A procedure should be in place to authorise maintenance activities and to identify any potential environmental impacts.</li> </ul>
<b>Environmental impacts</b>	All
<b>Costs</b>	Variable

<b>MT4</b>	<b>Process control</b>
<b>Pollutants</b>	All
<b>Description</b>	Control of the process is important to ensure that yields are optimised and the potential for waste arisings and accidents minimised.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• The process operator should be able to demonstrate that all key indicators of process performance have been identified and that they are adequately monitored;</li> <li>• Records should be kept of performance and should be used as the basis for the long term optimisation of the process.</li> </ul>
<b>Environmental impacts</b>	All
<b>Costs</b>	Variable

<b>MT5</b>	<b>Waste minimisation</b>
<b>Pollutants</b>	All
<b>Description</b>	Waste minimisation is an important element of preventing and minimising pollution at source.
<b>Availability</b>	The 3Es methodology Regional Waste Minimisation Clubs IChemE Guidance
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• Waste minimisation audits should be undertaken to a defined programme.</li> <li>• There should be active monitoring of materials throughput and mass balances should be constructed for water, energy, heat and solvent use</li> </ul>
<b>Environmental impacts</b>	All
<b>Costs</b>	Variable, but costs will often be balanced by savings

<b>MT6</b>	<b>Process and product design</b>
<b>Pollutants</b>	All
<b>Description</b>	Good design of a process or product is usually the most effective and efficient way of preventing and minimising pollution.
<b>Availability</b>	Developing
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• Consideration of potential environmental impacts should be undertaken at the very beginning of the design of a new process or product;</li> <li>• Alternative designs should be identified in a imaginative manner and their respective environmental impacts compared and contrasted;</li> <li>• At all key stages in the design procedure when consideration is given to whether or not to proceed with a project, environmental impact should be a key influence on decision making;</li> <li>• There should be an audit trail for the whole design procedure, clearly identifying the decisions reached, the information used and any assumptions that had to be made.</li> </ul>
<b>Environmental impacts</b>	All
<b>Costs</b>	Variable

<b>MT7</b>	<b>Staff awareness and training</b>
<b>Pollutants</b>	All
<b>Description</b>	Without staff support and understanding no management, process or abatement technique will ever be truly effective in preventing and minimising pollution.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• All staff should be made aware of the existence of the IPC authorisation and its implications for the operation of the process and, if relevant, wider site;</li> <li>• Specific training should be provided for all staff whose actions may have a significant impact on the environment;</li> <li>• Staff training and awareness should be regularly reviewed to ensure it is up to date and relevant. To this end records should be kept for all staff.</li> </ul>
<b>Environmental impacts</b>	All
<b>Costs</b>	Variable

<b>MT8</b>	<b>Finance and accounting</b>
<b>Pollutants</b>	All
<b>Description</b>	The economic implications of the environmental impacts of a process are a powerful motivating force for the process operator and they should be clearly understood.
<b>Availability</b>	Developing
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• There should be a good understanding of the costs associated with waste production. As far as possible the costs of environmental impacts should be attributed to the activities that give rise to them. This should be possible in most cases for the process, it may, however, be more difficult to attribute detailed costs to specific batches.</li> <li>• The financial implications of operating the management, process and abatement techniques associated with the process should be clearly understood. The process operator should be able to demonstrate that adequate resources have been assigned to each task</li> </ul>
<b>Environmental impacts</b>	All
<b>Costs</b>	Variable

<b>MT9</b>	<b>Incidents</b>
<b>Pollutants</b>	All
<b>Description</b>	Incidents, however infrequent and however brief, have the capability to cause significantly more harm than long term, routine releases.
<b>Availability</b>	High
<b>Operating performance</b>	<p>The operator should have in place:</p> <ul style="list-style-type: none"> <li>• well defined and tested procedures for responding to incidents. Staff should be aware of the steps they should take to minimise adverse environmental impact;</li> <li>• a clear and well understood procedure for reporting incidents internally;</li> <li>• a clear understanding with the Agency as to what constitutes a reportable incident;</li> <li>• a procedure for identifying the causes of incidents and undertaking improvements to ensure that they are not repeated.</li> </ul>
<b>Environmental impacts</b>	All
<b>Costs</b>	Variable



## PROCESS TECHNIQUES

<b>PST1</b>	<b>Drainage systems</b>
<b>Pollutants</b>	All
<b>Description</b>	Drainage systems are an important potential conduit to the environment
<b>Availability</b>	High
<b>Operating performance</b>	<p>As far as practicable effluent and drainage systems should be kept separate in order to minimise the amount of effluent requiring treatment. Separate systems should also be marked to differentiate them, particularly entry points.</p> <p>Unless special precautions have been taken it should be presumed that all underground drainage systems leak. Maintenance and leak detection programmes should be developed based on the chemicals that could potentially end up in the system and the proximity to sensitive ground and surface waters</p> <p>On multi-user sites responsibilities for the various sections of the site drainage system should be clearly delineated and someone should take an overview of its overall operation</p>
<b>Environmental impacts</b>	Spills and leaks can be mobilised by drainage systems and released to the environment
<b>Costs</b>	Variable

<b>PST2</b>	<b>Dry storage</b>
<b>Pollutants</b>	All
<b>Description</b>	Dry storage will be practised at most processes in the sector. It may range from relatively small holdings of a few chemicals to substantial holdings of a large number.
<b>Availability</b>	High
<b>Operating performance</b>	<p>Clear procedures should be implemented to promptly deal with leaks and spills. As far as possible spills/leaks should be recovered for reuse, where this is not possible clearly defined disposal routes should be available.</p> <p>Cleaning operations should minimise the amount of water used and should be directed to the site effluent system</p> <p>Risk assessment should be used to identify the level and type of bunding that should be installed to retain major spills and fire fighting water.</p>
<b>Environmental impacts</b>	There is the potential for cleaning operations to mobilise spills or for fire fighting water to mobilise the entire inventory
<b>Costs</b>	Variable

<b>PST3</b>	<b>Drum storage</b>
<b>Pollutants</b>	All
<b>Description</b>	Drum storage is an integral part of the operation of most processes in the sector.
<b>Availability</b>	High
<b>Operating performance</b>	<p>Bulk drum storage should generally be on a kerbed or bunded, concrete hardstand. This area should drain to the site effluent treatment system or, preferably, to a holding tank where the contents can be periodically monitored prior to deciding whether treatment is required.</p> <p>Drums will have to be distributed from the bulk storage area prior to use. This secondary storage should be minimised as far as possible. Where it does occur provision should be taken to protect the drums from traffic movements. Storage close to access points to drainage systems should be minimised.</p> <p>Drums should be clearly labelled with their contents and use by date.</p> <p>Spent drums should not be allowed to accumulate. As far as possible they should be cleaned and reused, although product quality control requirements may preclude this. Where cleaning occurs on site the potential environmental impacts should be addressed. Where this is not feasible specialist contractors should be used</p>
<b>Environmental impacts</b>	<p>There is a relatively low risk of spills from drum storage and handling.</p> <p>Drum cleaning operations may give rise to releases to the environment</p>
<b>Costs</b>	Variable

<b>PST4</b>	<b>Tank storage</b>
<b>Pollutants</b>	All
<b>Description</b>	Tank storage is an integral part of the operation of most processes in the sector.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>In general tanks should have bunding with capacity to hold 110% of the contents of the largest tank. Risk assessment should be used to demonstrate where this requirement may be inadequate or unduly onerous.</p> <p>Risk assessment should also be used to demonstrate whether high level alarms or other types of monitoring device are required to detect leaks or spills during loading/unloading.</p> <p>It is usually inappropriate to have penetrations in the bunding. Rainwater should not be allowed to accumulate in the bottom of the bund. It should be pumped out directly to the effluent system or, preferably, held and monitored to see if treatment is required.</p> <p>Where the stored liquid presents a fire hazard consideration should be given to the potential volume of fire fighting water that may have to be used and how this would be held on site</p>
<b>Environmental impacts</b>	<p>Releases to surface and ground water</p> <p>Land contamination</p>
<b>Costs</b>	Variable

<b>PST5</b>	<b>Tanker loading and off-loading</b>
<b>Pollutants</b>	All
<b>Description</b>	Tank storage is an integral part of the operation of most processes in the sector. The sector is characterised by the frequent loading and unloading of these tanks, usually by road tankers.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>Tanker loading/un-loading areas should be concreted and graded to a central drainage point. 'Sleeping policemen' can be a relatively simple way of bunding such areas.</p> <p>Drainage points should pass direct to the effluent system or, preferably, to a hold and monitor tank.</p> <p>Flexible hoses are a vulnerable point during loading/un-loading operations and procedures should be in place to ensure that they are correctly connected and regularly maintained.</p> <p>Loading/un-loading points should be protected from potential traffic accidents. This may involve the installation of physical barriers or procedural changes to route traffic movements away from the area.</p> <p>Potential fugitive emissions from tanks should be identified (e.g displacement losses due to filling, the use of inert gas blankets or variations in the ambient temperature)</p>
<b>Environmental impacts</b>	Storage tanks may give rise to longer term fugitive losses or short term accidental releases
<b>Costs</b>	Variable

<b>PSE1</b>	<b>Ventilation</b>
<b>Pollutants</b>	Volatile organic compounds
<b>Description</b>	Many processes in this sector are enclosed within buildings. These buildings may be vented for health and safety reasons
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>Where ventilation is used estimates of potential releases should be made. Where releases are considered to be significant consideration may need to be given to utilising techniques that minimise fugitive losses. Where this is still inadequate there may be a need for the collection of the vented air and its disposal via an abatement technique.</p> <p>Consideration may also need to be given to ventilation stacks and their potential to contaminate rainwater that flows across or collects on roofs.</p>
<b>Environmental impacts</b>	Releases to atmosphere
<b>Costs</b>	Variable

<b>PSE2</b>	<b>Leak detection and repair</b>
<b>Pollutants</b>	VOCs
<b>Description</b>	There is the potential for fugitive losses whenever VOCs are being used
<b>Availability</b>	Widespread
<b>Operating performance</b>	Fugitive losses may arise from all the activities covered by the PSE proformas. The operator should estimate potential fugitive losses and, where these are significant, introduce a leak detection and repair programme to minimise them
<b>Environmental impacts</b>	Releases to air
<b>Costs</b>	Variable

<b>PSE3</b>	<b>Over pressure</b>
<b>Pollutants</b>	All
<b>Description</b>	Many reactions in this sector are undertaken at elevated temperatures and/or pressures. There is always a possibility that abnormal operating conditions may cause over pressure in the reactor. For health, safety and environment reasons this over pressure needs to be dissipated as quickly as possible.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>For particularly hazardous reactions and/or chemicals it may be necessary to design inherent protection into the reactor e.g duplicated or triplicated alarm or trip mechanisms. This is an expensive option.</p> <p>Most reactors will make use of relief valves and/or bursting discs. Many variations are available e.g two valves in parallel, a low pressure one for small releases that is connected to an abatement technique and an unabated high pressure one that is vented direct to atmosphere. For particularly hazardous compounds it may be necessary to vent to a dump tank where most of the reactor contents can be held.</p>
<b>Environmental impacts</b>	Releases to air
<b>Costs</b>	Variable



<b>PSE4</b>	<b>Vacuum systems</b>
<b>Pollutants</b>	VOCs
<b>Description</b>	Vacuum systems are extensively used in the sector. There are a number of different options for raising a vacuum, all of which may have an environmental impact
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>The main techniques for raising a vacuum are:</p> <ul style="list-style-type: none"> <li>• steam jet ejectors - simple and cheap but use large amounts of water, create a contaminated effluent, give rise to atmospheric emissions of non-condensables and may cause a noise problem;</li> <li>• liquid ring pumps - as with steam jet ejectors but there are likely to be more options for treating or reusing/recycling the contaminated effluent;</li> <li>• rotating vane pumps/diaphragm pumps - these can achieve better vacuums than the above and generally have less of an environmental impact, although only if they are well maintained.</li> </ul>
<b>Environmental impacts</b>	<p>Fugitive releases of VOCs</p> <p>Waste water arisings</p>
<b>Costs</b>	Variable

<b>PSE5</b>	<b>Pumps</b>
<b>Pollutants</b>	All
<b>Description</b>	Pumps are an integral part of all processes in the sector. They are used for the transfer of liquids
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>In terms of their environmental impact pumps can be divided into those that leak all of the time, those which are liable to leak heavily on failure and those that never leak.</p> <p>Pumps based on reciprocating or rotating shafts need some kind of packing (seal) to prevent the process fluid escaping to the environment. A small amount of leakage will always occur with these pumps, although good maintenance can minimise losses.</p> <p>Double mechanical seals have been developed to further minimise these seal losses. They need to well maintained to operate effectively and if they fail can lead to a high leakage rate.</p> <p>Pumps have been developed that prevent all leakage, provided they are well maintained. These include magnetic drive centrifugal pumps, canned centrifugal pumps and diaphragm pumps</p>
<b>Environmental impacts</b>	Fugitive releases of VOCs
<b>Costs</b>	Variable

<b>PSE6</b>	<b>Gas compressors</b>
<b>Pollutants</b>	All
<b>Description</b>	Compressors are widely used for the transfer of gases
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>As with pumps, compressors have sealing arrangements to prevent the escape of process gases and the ingress of air. These arrangements are usually more difficult to organise for gases than for liquids and leaks will generally result in a larger release to the environment. Common types of seal include:</p> <ul style="list-style-type: none"> <li>• labyrinth - two sets of interlocking teeth, one rotating, one stationary;</li> <li>• restrictive seal - multiple stationary carbon rings;</li> <li>• mechanical seals - similar to those used in pumps;..</li> <li>• liquid film - liquid is injected into the space between two sets of tolerance bushes.</li> </ul> <p>Good maintenance is important to prevent releases</p>
<b>Environmental impacts</b>	Fugitive releases of VOCs.
<b>Costs</b>	Variable

<b>PSE7</b>	<b>Agitator systems</b>
<b>Pollutants</b>	VOCs
<b>Description</b>	Batch reactors require a stirring (agitating) system to ensure good mixing of the reagents
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>The main environmental concerns are that:</p> <ul style="list-style-type: none"> <li>• mixing is effective, ensuring good yields and minimising waste arisings</li> <li>• a good seal is maintained where the agitator enters the reactor. This minimises fugitive releases.</li> </ul> <p>In general releases from this source will be low and the need to deviate from the standard agitator system will be rare. Some alternatives include jet mixing, static mixers, vibrating mixers and gas sparging</p>
<b>Environmental impacts</b>	Fugitive releases of VOCs
<b>Costs</b>	Variable

<b>PSE8</b>	<b>Valves</b>
<b>Pollutants</b>	VOCs
<b>Description</b>	Valves allow the flow of fluid (liquid or gas) to be controlled or stopped.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>A typical process will have many hundreds of valves. The most common types are the:</p> <ul style="list-style-type: none"> <li>• gate valve - a flat sliding plate is inserted across the flow;</li> <li>• globe valve - a disc is lowered into the flow orifice;</li> <li>• plug or ball valves - a rotating plug with an aperture through it. The plug can be rotated so that the aperture is aligned or closed to the flow.</li> </ul> <p>The operating stem of the valve will be packed and as with pumps this will require maintenance to prevent leakage. Traditionally maintenance of valves may have been accorded a lower priority than that of other potential sources of fugitive emissions.</p> <p>Because of their contribution to the control of the process, valves should also be clearly addressed in operating procedures.</p>
<b>Environmental impacts</b>	Fugitive releases to air
<b>Costs</b>	Variable

<b>PSE9</b>	<b>Purging</b>
<b>Pollutants</b>	VOCs
<b>Description</b>	Batch operations require frequent purging to allow entry to vessels and their preparation for a new batch and/or campaign.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>Purging may be by air or, where there is a risk of a flammable atmosphere or reagents react with air, inert gas. There are two main options:</p> <ul style="list-style-type: none"> <li>• once through purging - directs a constant stream of air/inert gas through the system;</li> <li>• pressure purging - a fixed volume of air/inert gas is added to the vessel under pressure and then released. This may be repeated several times</li> </ul> <p>Pressure purging may offer greater control over the volume of air/inert gas used.</p>
<b>Environmental impacts</b>	Releases to air
<b>Costs</b>	Variable

<b>PSE10</b>	<b>Leakage</b>
<b>Pollutants</b>	Corrosive compounds
<b>Description</b>	Heating and cooling systems are widely used. Many have the potential to leak
<b>Availability</b>	Widespread
<b>Operating performance</b>	Good maintenance and operating procedures are required to prevent leakage between process and heating/cooling systems. Corrosion monitoring may be required; Leak detection may be required
<b>Environmental impacts</b>	Waste water arisings
<b>Costs</b>	Variable

<b>PRI</b>	<b>Reactor</b>
<b>Pollutants</b>	All
<b>Description</b>	Reactors are extensively used in the sector. They provide the necessary flexibility to deal with a wide range of products, production volumes and campaign durations
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>The operator may be expected to address the following points:</p> <ul style="list-style-type: none"> <li>• what impurities are there in the raw material feed and what are their implications for waste arisings?</li> <li>• what side reactions are there and how may they reduce yields?</li> <li>• can reagents, solvents catalysts, temperature and pressure be optimised to minimise waste;</li> <li>• can catalyst be recovered and, if so, can it be reused?</li> <li>• is the order in which reagents added optimal for waste minimisation?</li> <li>• can the use of relief valves be minimised by improving the design of the reactor?</li> <li>• can reactions conditions be better controlled to minimise wastes?</li> <li>• can off specification materials be recovered and reused?</li> <li>• is the floor area beneath the reactor chemically impermeable and kerbed?</li> <li>• is the reactor designed to allow effective cleaning?</li> <li>• is it possible to sequence campaigns to minimise the need for cleaning; (this may be particularly difficult because of the high quality requirements of the sector)?</li> <li>• have the opportunities for recycling solvents to the reactor, for example by the use of condensers, been maximised?</li> </ul>
<b>Environmental impacts</b>	<p>Release to air</p> <p>Waste water arisings</p> <p>Solid waste arisings</p>
<b>Costs</b>	Variable



<b>PS1</b>	<b>Liquid-vapour separation</b>
<b>Pollutants</b>	All
<b>Description</b>	On completion of the reaction it may be necessary to separate a liquid from a vapour
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>The most commonly used liquid-vapour techniques are:</p> <ul style="list-style-type: none"> <li>• evaporation - potentially large energy requirements;</li> <li>• steam or air stripping - air stripping will usually have lower energy requirements but steam may be required for less volatile components;</li> <li>• distillation - potentially large energy requirements.</li> </ul> <p>The vapour will usually be condensed and it is therefore important that heat transfer surfaces are adequately sized and that the flow of any cooling liquid is monitored for loss of flow.</p>
<b>Environmental impacts</b>	<p>Releases to air</p> <p>Disposal of distillation bottoms</p>
<b>Costs</b>	Variable

<b>PS2</b>	<b>Liquid-liquid separation</b>
<b>Pollutants</b>	All
<b>Description</b>	On completion of the reaction it may be necessary to separate a liquid from a liquid
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>The most widely used liquid-liquid separation techniques are:</p> <ul style="list-style-type: none"> <li>• extraction with water or solvent - has the advantage of low energy requirements;</li> <li>• decantation - again low energy requirements but only useful for totally immiscible liquids;</li> <li>• centrifuging - potentially large energy requirements;</li> <li>• multi-stage contacting.</li> </ul> <p>Dust particles etc can affect separation. Identification of the boundary between two phases is the key to minimising waste arisings and an operator could be expected to demonstrate that this had been considered</p>
<b>Environmental impacts</b>	Waste water arisings
<b>Costs</b>	Variable

<b>PS3</b>	<b>Solid-liquid separation</b>
<b>Pollutants</b>	All
<b>Description</b>	On completion of the reaction it may be necessary to separate a solid from a liquid.
<b>Availability</b>	Widespread
<b>Operating performance</b>	<p>The main solid-liquid separation techniques are:</p> <ul style="list-style-type: none"> <li>• centrifuging;</li> <li>• filtration;</li> <li>• sedimentation/clarification;</li> <li>• drying.</li> </ul> <p>There is always the potential for solids breakthrough with filtration and some kind of warning system should be in place to deal with this;</p> <p>Wash waters will often be generated and steps should be taken to minimise these arisings.</p>
<b>Environmental impacts</b>	<p>Releases to air</p> <p>Solid waste arisings</p> <p>Waste water arisings</p>
<b>Costs</b>	Variable

<b>PP1</b>	<b>Liquid purification</b>
<b>Pollutants</b>	All
<b>Description</b>	After separation there may still be the need for a liquid purification stage
<b>Availability</b>	High
<b>Operating performance</b>	<p>Liquid products are usually purified by distillation. Sources of losses include:</p> <ul style="list-style-type: none"> <li>• entrained gas - a supplementary condensing area or the use of a cooler heat exchange fluid may minimise this;</li> <li>• ineffective recovery - more extraction or more reflux can be used to improve recovery. More modern packing or high efficiency trays can be used to achieve this.</li> </ul>
<b>Environmental impacts</b>	Liquid wastes Releases to air
<b>Costs</b>	Variable

<b>PP2</b>	<b>Solid purification</b>
<b>Pollutants</b>	All
<b>Description</b>	After separation there may still be the need for a solid purification stage
<b>Availability</b>	High
<b>Operating performance</b>	<p>This will usually consist of the separation of the solids from the mother liquor followed by washing and drying. There may also be a need for supplementary dissolving and crystallisation.</p> <p>Washing and crystallising activities have the potential to produce large volumes of dilute liquors - which can be expensive and difficult to treat or recover effectively</p> <p>Counter current systems should be used as far as possible to minimise water use and waste water arisings. This may necessitate the installation of additional holding tanks</p>
<b>Environmental impacts</b>	<p>Solid waste arisings</p> <p>Waste water arisings</p>
<b>Costs</b>	Variable

## AIR ABATEMENT TECHNIQUES

<b>AV 1</b>	<b>Activated carbon adsorption - General principles</b>
<b>Pollutants</b>	VOCs: alcohols, ketones, aromatics, aldehydes, esters, chlorinated hydrocarbons
<b>Description</b>	A wide range of adsorbents and techniques for supporting the adsorbent are available. As it is by far the most widely used adsorbent in this sector, only activated carbon is discussed below. A1.1, 1.2, 1.3 and 1.4 summarise the four main ways of supporting the activated carbon - fixed bed, fluidised bed, continuous and canisters, respectively.
<b>Availability</b>	<p>The technique has been widely utilised and demonstrated over a wide range of operating conditions.</p> <p>There are a wide variety of options for modifying the technique to deal with specific waste streams. For example beds may be constructed out of a wide range of materials and can also be coated in a specific chemical to enhance the recovery of particular pollutants. In addition, small drum beds are available that can be fitted relatively cheaply and easily to small, homogenous waste streams</p>
<b>Operating performance</b>	<p>Capable of achieving particularly low release levels, removal efficiencies approaching 99% achievable but these levels require optimum operating conditions i.e:</p> <p>Optimum operating performance requires:</p> <ul style="list-style-type: none"> <li>• only a few VOCs in the gas stream, preferably with similar adsorption characteristics;</li> <li>• particulate and moisture free streams (both of which may 'blind' adsorption points on the bed);</li> <li>• gas stream temperatures below 30°C (this increases residence time in the bed);</li> <li>• low gas stream velocities (this increases residence time in the bed);</li> <li>• pollutants with a molecular mass (MM) in the range 45 -140 (lower MMs have poor carbon affinity, higher MMs may be difficult to desorb);</li> <li>• compounds with a low polarity, cyclic rather than linear and unsaturated rather than saturated;</li> <li>• ensuring that beds are thoroughly dried and cooled after regeneration. Regenerated beds must be conditioned with hot air;</li> <li>• beds need to be cooled and dried before being returned to operation after regeneration.</li> </ul>
<b>Environmental impacts</b>	<p>Regeneration of beds dealing with homogenous waste streams offers recycling opportunities.</p> <p>Spent beds and waste streams from regeneration that cannot be recycled will require treatment and/or disposal.</p> <p>The only raw materials required during use of the beds is steam or air for regeneration purposes. These will be contaminated with VOCs.</p> <p>Energy will be required for steam raising and potentially for reducing the velocity of the waste stream, cooling it down and removing particulates.</p>
<b>Costs</b>	

<b>AV 1.1</b>	<b>Fixed bed adsorption</b>
<b>Pollutants</b>	VOCs and odours
<b>Description</b>	Waste gas is passed through a stationary bed of adsorbent. Normally two beds operated are in parallel with one adsorbing and the other regenerating.
<b>Availability</b>	The simplest and by far the most common adsorption system.
<b>Operating performance</b>	<p>Advantages:</p> <ul style="list-style-type: none"> <li>• simple and economical;</li> <li>• infrequent handling of solid adsorbent;</li> <li>• recycling opportunities..</li> </ul> <p>Disadvantages:</p> <ul style="list-style-type: none"> <li>• high contaminant levels saturate and render inactive a large proportion of the bed;</li> <li>• large beds needed for high adsorbate flow rates.</li> </ul> <p>If regeneration and adsorption stages are of differing duration, it may be necessary to employ multiple beds.</p> <p>If pressure drop across bed is too high, adsorbent may abrade and bed may channel. Thus, beds are often compartmentalised.</p> <p>Pressure drop inversely proportional to adsorbent particle size but large adsorbent particles have poor efficiency due to lower surface area.</p>
<b>Environmental impacts</b>	Disposal of spent adsorbent; Further treatment of regeneration stream and disposal or recycling of VOCs required;
<b>Costs</b>	

<b>AV 1.2</b>	<b>Fluidised bed adsorption</b>
<b>Pollutants</b>	VOCs and odours
<b>Description</b>	A continuous process in which VOC-laden air flows upwards through perforated trays containing adsorbent. Regenerated adsorbent is fed to the top tray from where it falls downwards from tray to tray, to a desorber before being transported back to the top of the system.
<b>Availability</b>	Medium
<b>Operating performance</b>	<p>Advantages:</p> <ul style="list-style-type: none"> <li>• multi-stage continuous process;</li> <li>• recycling opportunities.</li> </ul> <p>Disadvantages:</p> <ul style="list-style-type: none"> <li>• more complex than fixed bed systems;</li> <li>• expense of handling and transport of solids;</li> <li>• solids handling equipment prone to mechanical malfunction;</li> <li>• system must be large to be economical;</li> <li>• attrition of adsorbent and higher 'top-up' costs;</li> <li>• require a large volume of adsorbent.</li> </ul>
<b>Environmental impacts</b>	<ul style="list-style-type: none"> <li>• Disposal of spent adsorbent;</li> <li>• Further treatment of regeneration stream and disposal or recycling of VOCs;</li> <li>• Particles of adsorbent may become entrained in the exhaust stream.</li> </ul>
<b>Costs</b>	



<b>AV 1.3</b>	<b>Continuous moving bed adsorption</b>
<b>Pollutants</b>	VOCs and odours
<b>Description</b>	<p>A continuous system may consist of :</p> <ul style="list-style-type: none"> <li>• the adsorbent falling by gravity through the rising gas stream in a column before passing through a regeneration stage and then back to the top of the column.</li> <li>• a large drum of adsorbent rotating at 1 - 2 revolutions per hour passing through successive zones where adsorption, regeneration and drying/cooling take place.</li> </ul>
<b>Availability</b>	Medium
<b>Operating performance</b>	Advantages/disadvantages as for fluidised bed systems (AV1.2)
<b>Environmental impacts</b>	Disposal of spent adsorbent; Further treatment of regeneration stream and disposal or recycling of VOCs.
<b>Costs</b>	

<b>AV 1.4</b>	<b>Canisters</b>
<b>Pollutants</b>	VOCs and odours.
<b>Description</b>	Drum or canister mounted adsorbent can be easily and quickly retrofitted to low concentration/flow sources of VOCs
<b>Availability</b>	High
<b>Operating performance</b>	Usually used for flows less than 170 m <sup>3</sup> /hour and concentrations less than 1 ppm
<b>Environmental impacts</b>	Regeneration and recycling is not usually undertaken and the spent canisters must be disposed of.
<b>Costs</b>	Low

<b>AV 2.1</b>	<b>Coolant/refrigerant condensation</b>
<b>Pollutants</b>	VOCs
<b>Description</b>	<p>Shell-and-tube condensors offer indirect cooling in which solvent condensation occurs on the cold shell side of the tubes from where it drains for collection or re-use.</p> <p>Spiral heat exchangers operate in a similar way; they are more expensive but have a number of advantages (e.g. high turbulence, self-cleaning, efficiency maintained with a smaller unit/cooling area).</p> <p>Direct condensation operates by intimate mixing of the gas stream with a cooled liquid; it suffers from the disadvantage that it requires an additional separation stage.</p>
<b>Availability</b>	High
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• Wide range of operating conditions with efficiencies from 50 to 95%.</li> <li>• Not normally applicable to concentrations below 10,000 ppm in the gas stream.</li> <li>• Can cope with flows up to 120,000 m<sup>3</sup>/hour.</li> <li>• Efficiency improves with lower temperature: operating temperatures as low as -62°C can be achieved depending on the design and coolant employed.</li> <li>• If moisture is present in the gas stream, ice may form, reducing removal efficiencies.</li> </ul> <p>US EPA (1978) recommend that for VOC control the following temperatures must be achieved for compounds with a particular vapour pressure:</p> <ul style="list-style-type: none"> <li>• -25°C for vapour pressure &gt; 40kPa (20°C);</li> <li>• -15°C for vapour pressure &gt; 20kPa (20°C);</li> <li>• 0°C for vapour pressure &gt; 10kPa (20°C);</li> <li>• 10°C for vapour pressure &gt; 7kPa (20°C);</li> <li>• 25°C for vapour pressure &gt; 3.5kPa (20°C);</li> </ul> <p>Safety features should include:</p> <ul style="list-style-type: none"> <li>• temperature alarms for exit coolant and vent;</li> <li>• flow sensors on condenser inlet and vent stream;</li> <li>• concentration monitor in vent stream;</li> <li>• select lowest practicable coolant temperature;</li> <li>• when refluxing, condenser cooling capacity should exceed reaction vessel heating capacity.</li> </ul>
<b>Environmental impacts</b>	<ul style="list-style-type: none"> <li>• provides the option for re-cycling/re-using solvents, but disposal problems if re-use is impracticable;</li> <li>• high volatility solvents may be released to atmosphere without additional preventive measures;</li> <li>• residues (solid/liquid) require appropriate disposal;</li> <li>• condensate from direct contact condensers often may not be re-usable and create waste disposal problems.</li> <li>• Good Practice Guide CG89 (Environmental Technology Best Practice Programme) offers advice on improving energy efficiency of heat exchangers.</li> </ul>
<b>Costs</b>	<p>Most cost-effective control for VOCs except at low emission rates;</p> <p>Higher energy costs for operation at low temperatures.</p>

<b>AV 2.2</b>	<b>Cryogenic condensation</b>
<b>Pollutants</b>	VOCs
<b>Description</b>	Condensation at extremely low temperatures using liquid nitrogen as the refrigerant.
<b>Availability</b>	Low
<b>Operating performance</b>	<p>Liquid nitrogen is an ideal low temperature coolant because it:</p> <ul style="list-style-type: none"> <li>• has a low boiling point (-196°C);</li> <li>• is non-toxic;</li> <li>• is non-corrosive;</li> <li>• is non-flammable.</li> </ul> <p>It may be particularly appropriate to use it at sites where liquid nitrogen is already used for other purposes in amounts that balance with the needs of the abatement system;</p> <p>Normally, a pre-condenser (chilled water or glycol) is used to maximise efficiency;</p> <p>Operating efficiencies of better than 99% are practicable and in theory any VOC may be removed from the gas stream;</p> <p>The operating temperature can be adjusted to deal with new VOCs or revised release limits;</p> <p>When ice formation becomes a problem, a cool/thaw continuous cycle offers benefits. The recovered solvent should be low in water and be suitable for immediate re-use.</p> <p>Indirect cooling using steel balls pre-cooled in liquid nitrogen has been introduced recently.</p>
<b>Environmental impacts</b>	<p>Provides the option for re-cycling/re-using solvents, but disposal problems if re-use is impracticable.</p> <p>If nitrogen is not used on site or is currently used but not in sufficient amounts to facilitate abatement then energy requirements may be increased.</p>
<b>Costs</b>	High capital and operating costs.

<b>AV 3.1</b>	<b>Flares</b>
<b>Pollutants</b>	Flammable gases and vapours (VOCs)
<b>Description</b>	Smokeless burners for the direct combustion of intermittent or emergency emissions or for the disposal of large volumes of combustible gas.
<b>Availability</b>	Elevated or ground level flares are commonly used in the petrochemical industry but much less frequently in this sector.
<b>Operating performance</b>	<p>The technique is difficult to control.</p> <p>Efficiency of combustion requires control of temperature and residence time, and turbulent mixing.</p> <p>Steam injection may aid combustion and reduce polymerisation.</p> <p>Not suited to low gas flow rates.</p>
<b>Environmental impacts</b>	<p>Generation of heat which is wasted.</p> <p>May be a nuisance in terms of light and noise.</p> <p>Risk of incomplete combustion.</p> <p>Poor control may lead to emission of toxic materials or smoke.</p> <p>Not viable for halogenated compounds.</p> <p>May require use of supplementary fuels.</p>
<b>Costs</b>	Low cost.

<b>AV 3.2</b>	<b>Thermal oxidation</b>
<b>Pollutants</b>	VOCs (especially solvents) and odours
<b>Description</b>	Waste gases, usually pre-heated by the hot combustion gases, are passed into a combustion chamber. If the gases are VOC-rich with a calorific value $>20\text{MJ/Nm}^3$ , they may be burnt without auxiliary fuels, although these may be required for process start-up, shut-down and in emergencies.
<b>Availability</b>	Widely used control measure applicable to any concentration of VOC when flow fluctuations are low, but less effective at high flows/low concentrations.
<b>Operating performance</b>	<p>Performance depends on three variables:</p> <ul style="list-style-type: none"> <li>• residence time;</li> <li>• operating temperature - typically <math>200\text{--}400^\circ\text{C}</math> above the auto-ignition temperature;</li> <li>• turbulence - necessary to provide good heat and mass transfer in the combustion zone. Achieved by burner design and baffles within combustion chamber.</li> </ul> <p>Useful energy can be recovered from oxidation by:</p> <ul style="list-style-type: none"> <li>• 'Recuperative' systems applicable to high VOC concentrations at low flow rates - exhaust gas heats incoming gas through heat exchangers.</li> <li>• 'Regenerative' systems applicable to low concentrations in high flow rates - exhaust gases pass through ceramic beds which, on flow reversal, are used to heat incoming gas.</li> </ul> <p>Usually inappropriate at flows <math>&lt;55\text{m}^3/\text{min}</math>.  Cost-effective compared to alternative control measures but this decreases at high emission rates. Control of halogenated compounds significantly more expensive than non-halogenated.  Unsuitable for lead-alkyls due to lead fouling.</p>
<b>Environmental impacts</b>	<p>Most systems require high secondary fuel use, especially if VOC content of waste steam is insufficient for efficient combustion;</p> <p>Incomplete combustion results in the formation of new pollutants such as aldehydes and organic acids; S and Cl compounds may produce <math>\text{SO}_2</math> and HCl, respectively, requiring the application of a scrubber with its own waste disposal needs. Process control important in minimising <math>\text{NO}_x</math> formation.</p>
<b>Costs</b>	Installation costs high; running costs dependent on secondary fuel usage.

<b>AV 3.3</b>	<b>Catalytic oxidation</b>
<b>Pollutants</b>	VOCs and other oxidisable vapour-phase pollutants.
<b>Description</b>	An oxidiser in which a catalyst is employed to reduce the temperature at which destruction occurs. Vent gases are passed into a mixing chamber containing a catalyst supported on an inert substrate which is heated to ca. 320°C by the hot combustion products of the auxillary burners. This permits faster oxidation at lower temperatures than can be achieved in a thermal oxidiser. The most frequently used catalysts are Pt and Pd; Co, Cr, Cu, Ni and V are also used. Catalysts reduce the likelihood of NO <sub>x</sub> formation.
<b>Availability</b>	Wide range of industrial applications.
<b>Operating performance</b>	<p>The following factors affect performance:</p> <ul style="list-style-type: none"> <li>operating temperature - typically range between 250 to 400°C, but must not exceed thermal resistance temperature of bed (ca. 700°C)</li> <li>space velocity - (volumetric flow ÷ bed volume): 40,000 bed volumes/h sufficient for 90% destruction efficiency; 30,000 bed volumes/h should give &gt;95% destruction efficiency.</li> <li>solvent concentration and properties: <ul style="list-style-type: none"> <li>- solvent concentration must not exceed that at which heat generated exceeds catalytic operating temperature;</li> <li>- stable solvents require higher pre-heat temperatures which reduces maximum tolerable solvent concentration.</li> </ul> </li> <li>catalyst characteristics - precious metal catalysts permit lower operating temperatures and higher space volumes. Typical catalyst quantities: <ul style="list-style-type: none"> <li>- precious metals: 0.025 to 0.05 m<sup>3</sup>/1000Nm<sup>3</sup>/h waste gas;</li> <li>- base metals: 0.07 to 0.1 m<sup>3</sup>/1000Nm<sup>3</sup>/h waste gas.</li> </ul> </li> <li>catalyst poisons and masking agents: <ul style="list-style-type: none"> <li>- P, Bi, As, Sb, Pb, Hg rapidly poison catalyst;</li> <li>- Fe, Sn, Si slowly poison catalyst;</li> <li>- S, halogens, Zn are reversible inhibitors;</li> <li>- organic solids reversibly coat active surfaces;</li> <li>- inert particulates coat and may erode catalyst surfaces.</li> </ul> </li> </ul> <p>Fluidised bed systems with constant replacement of catalyst reduce problems due to poisoning but require top up and may result in particulates being entrained in the exhaust stream.</p> <p>Sensitive to inlet flow fluctuations.</p> <p>Temperature/inlet flow monitors needed to ensure operation to specification.</p>
<b>Environmental impacts</b>	<p>Liberate CO<sub>2</sub>, H<sub>2</sub>O and heat, but latter can be recovered or recycled by employing dual bed reactors in series and reversing waste stream flow when second bed becomes too hot to absorb further heat;</p> <p>Fuel requirements lower (ca. 40-60%) than thermal oxidisers.</p> <p>Disposal of spent catalyst.</p>
<b>Costs</b>	<p>Relatively high capital costs; catalysts replacement costs may be high.</p> <p>Not cost-effective for high air flows with low combustibles content.</p>

AV 4	Biological oxidation
Description:	<p>Biological processes trap and oxidise (biodegrade) pollutants in a gas stream. Micro-organisms in an aqueous medium are brought into contact with the gasstream. Contaminant gases dissolve in the water and are biodegraded to less harmful compounds (idealy CO<sub>2</sub> and H<sub>2</sub>O) which pass into the exhaust air. The technique is best suited to low concentrations of readily biodegradable contaminants, and is often suitable for the control of odours.</p> <p><b>AV 5.1 - Biofiltration</b></p> <p>Biofilters can be sub-didided into two types:</p> <ul style="list-style-type: none"> <li>• <b>Soil-based</b> biofilters comprise a layer of soil underlain by a network of perforated pipes through which the waste gases are blown. Natural organisms within the soil (which tend to self-select according to the composition of the waste stream) biodegrade the contaminants. It is necessary to keep the soil lightly irrigated with water.</li> <li>• <b>Non soil-based biofilters</b> consist of a supporting layer of peat, heather, woodchip waste or, in some countries, domestic waste on which the microbial population develops. As with soil-based biofilters, it is essential to keep the bed irrigated though over-watering is detrimental.</li> </ul>
	<p><b>AV 5.2 - Bioscrubbing</b></p> <p>Bioscrubbers operate by passing the contaminated gas up a tower countercurrent to a flow of water containing a microbial population. The tower contains a packing material such as pall rings on which a microbial mat is formed. As with biofilters, the microorganisms biodegrade the contaminants.</p> <p><b>AV 5.3 - Bioreactor</b></p> <p>The micro-oragnisms are supported on an artificial substrate in a reactor.</p>
Availability	Medium
Operating performance	<p>Theoretically applicable to any VOC; Small molecules (&lt;7 C atoms) containing oxygen degraed readily.</p> <p>Optimal operation requires:</p> <ul style="list-style-type: none"> <li>• adequate residence time;</li> <li>• critical control of moisture content of bed (may need irrigation);</li> <li>• moderate temperatures (normally 15-30°, hot gases need to be cooled);</li> <li>• efficiency impaired at low temperatures;</li> <li>• high oxygen content;</li> <li>• presence of nutrients (N, P, Fe);</li> <li>• removal of fine particulate dusts;</li> <li>• prone to poisoning by toxic substances.</li> <li>• inhibited by certain toxic gases (H<sub>2</sub>S, CO), acids, heavy metals, and CN.</li> </ul> <p>Typically, for soil-based systems, gas flows are typically 5-25 m<sup>3</sup>/s. and a residence time of 5 mins. will require a bed area of 1,500-7,00 m<sup>2</sup>. Odour removal efficiencies &gt;99% achievable.</p> <p>Best suited to water-soluble pollutants</p>



<b>Environmental impacts</b>	<p>During and following start-up, efficiency is normally impaired until the substrate have been adequately colonised with microorganisms.</p> <p>Breakdown products are normally water and carbon dioxide.</p> <p>Some techniques use peat as substrate; extraction of peat is generally regarded to be environmentally undesirable.</p>
<b>Costs</b>	<p>Capital and operating costs generally low. Low energy requirements.</p>

**Description:**

Absorption is a process involving the mass transfer between gas and liquid phases in a device designed to promote intimate mixing between phases. The technique may involve a chemical reaction. In this case, recycling is not possible but the reaction product may have a beneficial use. The technique is also called "wet scrubbing", which is used for the removal of particulates, droplets and aerosols (see AP 1). In general the same scrubber cannot be used for the removal of both VOCs and particulates.

There are two essential factors which control process efficiency:

- effective contact between the gas and liquid phases;
- the concentration gradient.

Effective contact is increased by maximising the surface area of the absorbant by ensuring a small droplet size or coating the liquid on a high surface area packing material. The concentration gradient is influenced by gas and liquid flow rates, gas temperature, pressure drop and in some cases, droplet size.

There are two basic types of absorption process:

- a) 'liquid phase controlled' in which the gas is bubbled through the liquid, and
- b) 'gas phase controlled' in which the liquid is sprayed into the gas.

The main scrubber designs are summarised in AV 5.1-5.5.

**General comments on absorbants:**

Absorbants may be aqueous or non-aqueous liquids, the choice of which depends on the properties of the contaminant:

- water is suitable for soluble acid gases (e.g. HCl, HF, SiF<sub>6</sub>) and also NH<sub>3</sub>;
- alkaline solutions for less soluble acidic gasses (e.g. SO<sub>2</sub>, Cl<sub>2</sub>);
- acidic solutions for poorly soluble substances such as amines;
- oxidising solutions for controlling organic odours.

Organic solvents can be used for organic species but generate problems such as sludge formation and difficulties in separation of absorbent and solute.

Systems may be classified by gas solubility and reactivity. Trace gases can be classified as:

- very soluble - Henry's Law Constant = 1 atm/mol frac.;
- moderately soluble - Henry's Law Constant = 10 atm/mol frac.;
- relatively insoluble - Henry's Law Constant = 100 atm/mol frac.

Reagents may be incorporated into the liquid phase to enhance absorptive capacity; the reactions are classified as:

- rapid reaction - gas phase controlled, with absorbate diffusion into liquid phase the rate determining step;
- slow reaction - reaction is complete by the time the liquid is recycled;
- no reaction - liquid re-entering system is saturated with absorbate.

**Description:**

Scrubbers remove particulates and droplets from a gas stream by contact with a liquid. There are three main physical processes:

- a) Inertial impaction in which the gas stream flows round an obstruction while particles ( $>0.3 \mu\text{m}$  dia) of high momentum collide and adhere to the obstruction;
- b) Interception in which large particles within the gas stream touch and adhere to an obstruction; and
- c) Diffusional collection in which small randomly moving particles ( $<0.3 \mu\text{m}$  dia) strike and adhere to an obstruction.

The particles are removed by one of two processes:

- a) Wetted surface de-duster in which the obstructing surfaces are wetted and irrigated by a liquid which transports the particulate material, and
- b) Distributed liquid de-duster in which the collection liquid is itself sprayed as droplets into the gas stream.

*Many of the scrubbing processes employed for particulate and droplet removal are equally applicable to absorption of VOCs (see AV5), although it is rare that they can be optimised for both purposes*

<b>AV 5.1/AP 1.1</b>	<b>Packed column scrubbers</b>
<b>Pollutants</b>	VOCs, soluble gases and mists. Rarely used for particulates
<b>Description</b>	The scrubbing liquor and gas streams are pumped through a high surface area inert substrate (e.g. porecelain, plastic or metal) in a co-, cross- or counter-current manner. The purpose of the substrate is to provide a large surface area for contact between the two phases, so aiding intimate mixing.
<b>Availability</b>	High
<b>Operating performance</b>	<p>Best option when residence/contact time is critical.</p> <p>Performance can often be tailored by choice of scrubbing liquor to specific pollutants, e.g:</p> <ul style="list-style-type: none"> <li>• micro-organisms can be induced to grow on substrate using pollutant as energy source ('bioscrubbers'/'biofilters');</li> <li>• water will remove SO<sub>2</sub> with 99% efficiency;</li> <li>• sodium hydroxide brines will neutralise acidic impurities.</li> </ul> <p>Control of gas and scrubber flow essential to prevent wetting. Liquor flow alarm desirable. Also monitoring to ensure liquor composition remains within specification. Gradual deterioration in performance may be due to breakdown or uneven settling of packing and should be monitored via the pressure drop across the tower.</p> <p>Unsuitable for insoluble particulates which tend to block tower.</p> <p>Less efficient generally than plate towers, and less able to cope with pressure and flow fluctuations.</p>
<b>Environmental impacts</b>	Scrubbing liquors may be re-cycled, but will ultimately require disposal.
<b>Costs</b>	

<b>AV 5.2/AP 1.2</b>	<b>Plate tower scrubbers</b>
<b>Pollutants</b>	VOCs, odours and particulates
<b>Description</b>	<p>There are three variants on the basic designs, all of which provide intimate contact between the scrubbing and gas phases by passing the gas stream through a column of baffles down which the scrubbing liquor flows:</p> <ul style="list-style-type: none"> <li>• horizontal perforated plates (including bubble cap and venturi designs),</li> <li>• impingement plate (in which solid baffle plates are fixed above the perforated plates,</li> <li>• vertical plate (for odours).</li> </ul> <p>The movement of the gas causes frothing which aids the contact process.</p>
<b>Availability</b>	High
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• Operate in a counter-current manner with liquor flowing down column under gravity;</li> <li>• Rely on adequate contact time and efficient inter-phase contact;</li> <li>• Efficiency falls below 10 µm, and the limit for most designs is 1 µm;</li> <li>• Pressure drops typically range from 0.5-1.5 kPa with gas velocities of 18-30 m/s;</li> <li>• For particle scrubbing only, liquid-gas ratios can be as low as 0.27l/m<sup>3</sup>;</li> <li>• Suitable for the treatment of large volumes;</li> <li>• Better performance than packed towers, especially for particulates, and can cope better with flow and pressure fluctuations;</li> <li>• Impingement plate towers preferred for dilute gas streams, waste streams with high particulate loadings, and where low scrubber flow rates are desirable;</li> <li>• Can achieve high efficiencies, even for relatively insoluble pollutants;</li> <li>• Oxidising liquors may be used for odour control;</li> <li>• Should be fitted with flow alarms;</li> <li>• Exhaust gas may require de-misting.</li> </ul>
<b>Environmental impacts</b>	<p>High energy fans used to drive gas stream through tower. Disposal of spent scrubbing liquors.</p>
<b>Costs</b>	

<b>AV 5.3/AP 1.3</b>	<b>Fibrous packing scrubbers</b>
<b>Pollutants</b>	VOCs and particulates
<b>Description</b>	A chamber containing mats of fibrous material (typically glass, plastic or steel) which are sprayed with absorbant liquor. Waste gas flows horizontally or vertically through chamber. Mass transfer is acheived through contact with the wet fibres, while the main mechaism for particle removal is inertial impaction..
<b>Availability</b>	High
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• Efficiency per unit energy better than for packed absorbers;</li> <li>• Trace gas removal efficiency is generally &gt;90% and depends on gas and liquid flow rate, fibre diameter, cell thickness and distribution;</li> <li>• Typical gas velocities are 1.0-1.5 m/s with a pressure loss of 0.25-0.4 kPa across a 10 cm cell;</li> <li>• The liquid to gas flow ratio is typically 1.3-5.3 l/s per m<sup>3</sup>/s gas.</li> <li>• Problems encountered include: <ul style="list-style-type: none"> <li>• blockage of spray nozzles;</li> <li>• plugging of fibre mats;</li> <li>• insufficient irrigation.</li> </ul> </li> </ul>
<b>Environmental impacts</b>	Disposal of scrubbing liquid
<b>Costs</b>	

<b>AV 5.4/AP 1.4</b>	<b>Moving (or fluidised) bed scrubbers</b>
<b>Pollutants</b>	Volatiles and particulates
<b>Description</b>	Comprises a lightweight substrate supported on grids which are fluidised by the gas stream with a counter-current of scrubbing liquor. The intimate mixing of gas and scrubber liquid over the high substrate surface area permits efficient VOC absorption and removal of particulates. The latter do not block the bed because of its fluid motion.
<b>Availability</b>	High
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• scrubbing liquors may be chosen for particular applications (e.g. H<sub>2</sub>SO<sub>4</sub>, NaOH, H<sub>2</sub>O);</li> <li>• will remove 90% of particulates of dia. &gt;1 µm;</li> <li>• capable of simultaneous removal of particulates and trace gases with efficiencies approaching &gt;90% and 99% respectively;</li> <li>• typical gas velocities are 2.5 m/s with liquid/gas ratios ranging from 5x10<sup>-4</sup> to 1x10<sup>-2</sup>. Pressure drops per stage are of the order of 1.0-1.5 kPa.</li> </ul>
<b>Environmental impacts</b>	<p>Produces a slurry which may be re-cycled or will require disposal.</p> <p>Moisture content of exhaust gas plume may cause visual nuisance.</p> <p>Low power consumption.</p>
<b>Costs</b>	Construction and operation more expensive than packed towers.

<b>AV 5.5/AV 1.5</b>	<b>Spray tower scrubbers</b>
<b>Pollutants</b>	VOCs, odours and particulates
<b>Description</b>	A tower in which the waste gas flow upwards or horizontally through a countercurrent, cross-current or co-current of scrubber liquid produced as at a series of nozzles.
<b>Availability</b>	High
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• efficiencies depend upon droplet size, gas velocity, liquid:gas ratio, and droplet trajectory. Efficiency improves with spray nozzle pressure (&gt;1400 to 2800 kPa), and liquid:gas ratios (4-13 l/m<sup>3</sup>). Spray droplets are typically 0.1-1 mm diameter;</li> <li>• less effective in removing VOCs than other forms of absorption systems - generally restricted to removal of high solubility gases such as SO<sub>2</sub> and NH<sub>3</sub>;</li> <li>• multi-stage systems often employed to improve mass-transfer;</li> <li>• pressure drop across a tower is usually 0.25-0.5 kPa, and a typical liquid:gas ratio is in the range 4-13 litres water/m<sup>3</sup> gas;</li> <li>• droplet diameter and distribution are critical design parameters - typically, droplets of diameter 200-400 µm needed for VOC removal;</li> <li>• spray nozzle plugging can be problematic.</li> </ul>
<b>Environmental impacts</b>	Disposal of scrubbing liquid
<b>Costs</b>	



<b>AP 1.6</b>	<b>Venturi scrubbers</b>
<b>Pollutants</b>	Particulates and droplets. Not commonly used for VOCs.
<b>Description</b>	A wet collection system in which a scrubbing liquor is intimately mixed with the gas stream by forcing either the gas or the liquor through a constriction. The mixture is then separated in either a cyclone or with a series of baffle plates. There are two basic types: low pressure-drop and high-pressure drop; the former are more suited to particles of a few microns diameter.
<b>Availability</b>	Widely used in many industries.
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• capable of removal of particles and droplets exceeding 0.1 <math>\mu\text{m}</math> dia.;</li> <li>• efficiencies &gt;98% for 1 <math>\mu\text{m}</math> particles;</li> <li>• efficiency depends on pressure drop across it. Pressures typically in the range 1-15 kPa;</li> <li>• Suitable for flammable vapours;</li> <li>• in some designs, can maintain efficiency during pressure fluctuation by varying the orifice dimensions;</li> <li>• can handle high temperature, moisture laden or corrosive gas streams, and aerosols;</li> <li>• equipment should be alarmed in case of failure; performance should be monitored by analysis of exhaust gas and scrubbing liquor;</li> <li>• self-cleaning with no moving parts;</li> <li>• compact and not prone to plugging.</li> </ul>
<b>Environmental impacts</b>	Liquors may be re-cycled but require disposal when spent. Moderately high energy usage.
<b>Costs</b>	Moderately high energy usage and operating costs; both increase with operating efficiency.

<b>AP 1.7</b>	<b>Impingement and entrainment scrubbers</b>
<b>Pollutants</b>	Particulates and droplets
<b>Description</b>	This is a self-induced spray scrubber in which the inlet gas stream is accelerated towards a liquid surface. On impact with the liquid, the gas flow is reversed and large particles are separated by inertial impaction. A fine droplet spray is formed which is separated from the gas phase by an entrainment separator (i.e. a series of baffles).
<b>Availability</b>	High
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• efficiency depends on energy transfer in the contact zone; hence high gas velocities and pressure drops are used;</li> <li>• gas velocity at impact are typically 30 m/s with pressure drops controlled within the range 1.0-5.0 kPa;</li> <li>• cut diameters vary from several microns for low velocity impingement to several tenths of a micron at high velocities.</li> </ul>
<b>Environmental impacts</b>	Disposal of scrubbing liquid
<b>Costs</b>	

<b>AP 1.8</b>	<b>Rotary scrubbers</b>
<b>Pollutants</b>	Pariculates, droplets, aerosols and (less commonly) traces of VOCs
<b>Description</b>	<p>There are two basic designs, both of which provide intimate contact between the scrubbing and gas phases :</p> <p>i) mops - a radial fibre brush with scrubbing liquor fed to the centre and which rotates at high speed in the gas stream,</p> <p>ii) rotary - a set of rotating rigid vanes with scrubbing liquor fed to the centre and atomised in the vortex providing intimate contact with the gas stream.</p>
<b>Availability</b>	
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>high collection efficiencies approaching 98% for particles of 3-4 <math>\mu\text{m}</math> dia; operate at high volumetric gas flow.</li> </ul>
<b>Environmental impacts</b>	<p>Liquors may be recycled but require disposal when spent.</p> <p>High energy use, but provide forward momentum to gas stream, reducing the energy needs of fans.</p>
<b>Costs</b>	High operating costs

<b>AP 1.9</b>	<b>Mist eliminators</b>
<b>Pollutants</b>	Mists and aerosols.
<b>Description</b>	Used to remove small droplets from gas streams, mist eliminators operate by surface impaction. They are constructed as overlapping baffles, packed inert fibres or layers of wire mesh and may be operated dry or with a minimal quantity of scrubbing liquor.
<b>Availability</b>	Can be incorporated into most types of wet scrubbers and vent lines
<b>Operating performance</b>	<p>Design dependent on droplet size;</p> <p>Efficiency of droplet removal depends on type:</p> <ul style="list-style-type: none"> <li>• baffles: 50 microns;</li> <li>• mesh: 15 microns;</li> <li>• packed fibres: 2-5 microns.</li> </ul> <p>Removal efficiencies up to 98%.</p>
<b>Environmental impacts</b>	Separated material (and scrubbing fluid) disposal; possibility of re-use.
<b>Costs</b>	Low cost

AP 2.1	Cyclones
Pollutants	Particulate matter and droplets
Description	<p>There are two main designs: In <b>straight-through cyclones</b>, the dust laden stream is forced through a vessel with a set of fixed vanes or impellers which impart a circular motion to the gas stream, forcing particles to the walls and out of the vessel. The <b>reverse flow cyclone</b> operates on a similar principle except that the gas stream passing up the vessel is induced into a vortex either by vanes or by passing the air tangentially into the vessel. Again radial forces induce particulates to the walls, after which they fall to a dust collection hopper.</p>
Availability	High
Operating performance	<p>Often used as a coarse pre-treatment. Key design criteria include particle size, particle density, and gas flow rate/volume.</p> <p>Classified by their performance:</p> <ul style="list-style-type: none"> <li>• low performance 50-80% collection efficiency</li> <li>• medium performance 80-95% collection efficiency</li> <li>• high performance 95-99% collection efficiency</li> </ul> <p>Dry cyclones are inappropriate for particles &lt;5µm, but agglomeration may extend applicability to 0.5µm.</p> <p>Require regular maintenance and performance monitoring.</p> <p>Installations for large gas volumes, high particle loadings, high velocities and elevated temperatures are best served by a bank of parallel units.</p>
Environmental impacts	Disposal of collected particulates
Costs	Low capital, running and maintenance costs

<b>AP 3.1</b>	<b>Electrostatic precipitators</b>
<b>Pollutants</b>	Particulates (smoke, fumes, dusts, aerosols, etc.)
<b>Description</b>	In an electrostatic precipitators (EPs) ,particles within a gas stream are charged by a high voltage (30,000 to 60,000V) and attracted to charged collection plates or tubes of opposite polarity. Aggregated particles are dislodged and removed by mechanical means or spraying.
<b>Availability</b>	
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• remove sub-micron particles;</li> <li>• can work at high temperature (to 400°C);</li> <li>• corona power 100-1000 W per m<sup>3</sup>/s;</li> <li>• collection efficiencies approach 99.5%;</li> <li>• best suited to particles with resistivity of 10<sup>8</sup> to 10<sup>11</sup> ohm-cm. Those with a greater resistivity disrupt the corona, while those of &lt;10<sup>8</sup> ohm-cm tend to stick on the plates increasing the chance of re-entrainment;</li> <li>• plate wire EPs most common for high gas flows;</li> <li>• flat plate EPs tend to be used for low gas flows (50-100 m<sup>3</sup>/s) containing particles of low mass median diameter (1-2 μm) and high resistivity;</li> <li>• two-stage EPs most common for small gas volumes (&lt;25 m<sup>3</sup>/s) and a high proportion of submicron particles such as smoke;</li> <li>• not normally applicable to low gas flows (&lt;10m<sup>3</sup>/sec) but generally insensitive to particle size;</li> <li>• fire risk if applied to flammable materials.</li> </ul>
<b>Environmental impacts</b>	<p>Wet precipitators generate effluents requiring disposal. Dust disposal from dry precipitators.</p> <p>Risk of fire and explosion.</p>
<b>Costs</b>	High capital cost, low operating costs.

<b>AP 4.1</b>	<b>Fabric or bag filters</b>
<b>Pollutants</b>	Particulate matter
<b>Description</b>	Woven or felted fabric bag through which gas streams are forced. Filtration occurs either in the bulk of the fabric due to impingement or through forces of inertia, or by the formation of a 'dust cake' through which further filtration occurs. Tubular or flat bags are generally suspended within a manifold in a baghouse
<b>Availability</b>	Very widely used for de-dusting operations such as freeze-drying, protection of conveyor systems and other manual handling systems, or for cleaning-up the vents from silos and tanks.
<b>Operating performance</b>	<p>Bag filters:</p> <ul style="list-style-type: none"> <li>• are capable of high collection efficiencies (99.5% for particles &gt;1µm) and will remove substantial proportion of particles as small as 0.01µm;</li> <li>• operate at low to moderate temperatures;</li> <li>• are not suited to moisture-laden or acidic, tarry or gummy gas flows (tendency to 'blind');</li> <li>• may require protection from explosion;</li> <li>• degrade in use;</li> <li>• require regular cleaning/maintenance;</li> <li>• need burst bag detection in sensitive installations.</li> </ul>
<b>Environmental impacts</b>	Generate solid waste on emptying (by mechanical or sonic shaking, oscillating or tapping, or by compressed air blow-down) for disposal by normally to landfill or by incineration unless suited to re-cycling.
<b>Costs</b>	Moderately expensive form of filtration.

<b>AP 4.2</b>	<b>Cartridge filters</b>
<b>Pollutants</b>	Particulate matter
<b>Description</b>	Cartridges comprise ceramic, metal fibre, plastic sinter (e.g. Teflon™) filtration material.
<b>Availability</b>	Frequently used to control dust in exhaust vents.
<b>Operating performance</b>	<ul style="list-style-type: none"> <li>• capable of operation at very high temperatures and sudden fluctuations in temperature;</li> <li>• very high removal efficiencies up to 99.9% (3µm) and 99.5% (0.5µm). Teflon™ based sinters: 99%, 5µm and 95%, 1µm.</li> </ul>
<b>Environmental impacts</b>	Generates solid waste for disposal by normally to landfill or by incineration.
<b>Costs</b>	Low installation costs.



## WASTE WATER TECHNIQUES

<b>PRT 1</b>	<b>Pre-treatment - Water insoluble compounds</b>
<b>Pollutants</b>	Water insoluble compounds
<b>Description</b>	Water insoluble compounds can be physically separated from the waste water by skimming
<b>Availability</b>	High
<b>Operating performance</b>	A wide range of separating devices are available, see American Petroleum Institute (API) guidance. Skimming devices should be regularly inspected and should generally be positioned as close as possible to the point of arising.
<b>Environmental impacts</b>	The separator will have to be periodically emptied and the contents either recycled or disposed of
<b>Costs</b>	Low

<b>PRT 2</b>	<b>Pre-treatment - Solids removal</b>
<b>Pollutants</b>	Solids
<b>Description</b>	Solids of a wide range of sizes may need to be removed from the waste water
<b>Availability</b>	High
<b>Operating performance</b>	<p>A wide range of techniques are available, these include:</p> <ul style="list-style-type: none"> <li>• sedimentation - coagulants and flocculants may be added to promote sedimentation;</li> <li>• flotation - is usually removed to remove solids with a density less than that of water. Coagulants and flocculants may be used to promote flotation. Dissolved air flotation (DAF) may be used to remove oily wastes;</li> <li>• filtration - usually consists of a deep bed of granular media (sand, anthracite, garnet etc) in an open top tank. The waste water is gravity fed through it. The filter needs to be periodically cleaned by backwashing;</li> <li>• evaporation - heat is applied to evaporate the waste water to leave a residual solid behind. It will tend to be used for solids that are hazardous;</li> <li>• crystallisation - would typically be used for the treatment of waste waters with a relatively low volume and containing hazardous substances.</li> </ul>
<b>Environmental impacts</b>	The removed solids will need to be disposed of
<b>Costs</b>	Low

<b>PRT 3</b>	<b>Pre-treatment - pH adjustment</b>
<b>Pollutants</b>	Solids and Metals
<b>Description</b>	pH can be adjusted by the addition of an acid or a base to induce the precipitation of heavy metals or to optimise biological, flocculation/coagulation techniques
<b>Availability</b>	High
<b>Operating performance</b>	<p>Many metal compounds have a minimum solubility at a certain pH and thus can be induced to precipitate out of solution. Different metals may have minimum solubilities at different pHs and thus precipitation of metal mixtures may be complex. In addition, other components of the waste water may result in the pH of the minimum solubility being changed.</p> <p>The most commonly used liquid pH adjuster are HCl (for acidic conditions) and sodium hydroxide or lime (for alkaline conditions).</p> <p>Reaction tanks, agitators, monitoring and control capability, pumps and storage tanks will be required.</p>
<b>Environmental impacts</b>	Gas may evolve during pH adjustment and this may volatilise organics
<b>Costs</b>	

<b>PRT 4</b>	<b>Pre-treatment - Equalisation</b>
<b>Pollutants</b>	Flow, temperature, pH
<b>Description</b>	Balancing tanks are used to hold and/or combine waste waters. They allow the <i>adjustment of flow, temperature or pH</i>
<b>Availability</b>	High
<b>Operating performance</b>	Balancing tanks may require mixing to prevent settlement of solids Care should be exercised when the waste water is held for a period of time that it does not become septic and cause odours
<b>Environmental impacts</b>	Potential odour formation
<b>Costs</b>	

<b>ST1</b>	<b>Special Treatment - Air stripping</b>
<b>Pollutants</b>	Volatile organic compounds
<b>Description</b>	A current of air is brought into close contact with the waste water. This causes volatile compounds to evaporate.
<b>Availability</b>	High
<b>Operating performance</b>	<p>Various techniques are available for contacting the current of air and the waste water. These include:</p> <ul style="list-style-type: none"> <li>• packed tower aeration - waste water is passed down through a packed tower as air is blown upwards;</li> <li>• spray aeration - waste water is ejected from nozzles as a fine spray;</li> <li>• diffusion - air is bubbled through the waste water.</li> </ul> <p>Air stripping also removes carbon dioxide from the waste water and thus increases the pH. In hard waters this may also cause increased scaling;</p> <p>Air stripping is likely to be more cost effective than adsorption at high concentrations.</p>
<b>Environmental impacts</b>	The volatilised organics will have to be captured for recovery or destruction
<b>Costs</b>	

<b>ST2</b>	<b>Special Treatment - Steam stripping</b>
<b>Pollutants</b>	VOCs, ammonia
<b>Description</b>	The waste water is brought into close contact with steam
<b>Availability</b>	Wide
<b>Operating performance</b>	Its higher energy requirements will mean that it is used less often than air stripping. it will tend to be used in situations where relatively involatile compounds are present.
<b>Environmental impacts</b>	Consideration will need to be given to the treatment and/or disposal of the compounds that are partitioned fro the waste water to the steam.
<b>Costs</b>	

<b>ST3</b>	<b>Special Treatment - Distillation</b>
<b>Pollutants</b>	Volatile organic compounds
<b>Description</b>	Distillation makes use of the different boiling points of compounds to selectively separate them from the waste water
<b>Availability</b>	Low
<b>Operating performance</b>	The technical feasibility and ultimately cost of utilising distillation will be dependent on the number of organic compounds and other contaminants that are present
<b>Environmental impacts</b>	Large energy requirements
<b>Costs</b>	

<b>ST4</b>	<b>Special Treatment - Wet air oxidation</b>
<b>Pollutants</b>	High COD wastes that are not bioegradable and not concentrated enough to incinerate
<b>Description</b>	Waste water is oxidised in a reactor under elevated temperature (177-315°C) and pressure (7-200 bar)
<b>Availability</b>	
<b>Operating performance</b>	Organic compounds are oxidised, in varying proportions, to CO <sub>2</sub> , water and simple oxygenated acids and aldehydes, which can be treated using a biological technique At COD concentrations greater than 10000 mg/l the reaction is autothermal. The technique can deal with COD concentrations greater than 100000 mg/l, although dilution may be required.
<b>Environmental impacts</b>	There may be a waste water that requires subsequent treatment Compared to incineration, no NO <sub>x</sub> or SO <sub>x</sub> is formed and there is no need for auxiliary fuel
<b>Costs</b>	



<b>ST5</b>	<b>Special Treatment - Super critical water oxidation</b>
<b>Pollutants</b>	High COD wastes that are not bioegradable and not concentrated enough to incinerate
<b>Description</b>	Waste water is heated to 374°C and pressurised to 221 bar. Under these conditions it becomes supercritical and decomposes organic compounds
<b>Availability</b>	Low
<b>Operating performance</b>	Organic compounds are almost totally destroyed Most inorganic salts are insoluble in super critical water and can cause fouling or erosion. Halides can also give rise to corrosion problems as they are convertd to acids
<b>Environmental impacts</b>	
<b>Costs</b>	

<b>ST6</b>	<b>Special Treatment - Chemical oxidation</b>
<b>Pollutants</b>	Dilute aqueous wastes containing non-biodegradable COD
<b>Description</b>	An oxidising agent is added to the waste water to oxidise the target chemical(s)
<b>Availability</b>	High
<b>Operating performance</b>	The oxidising agent may be a gas (e.g chlorine), a liquid (e.g hydrogen peroxide) or a solid (e.g potassium permanganate)
<b>Environmental impacts</b>	The waste water may still require further treatment, for example to remove any biodegradable COD created by the oxidation reaction.
<b>Costs</b>	

<b>CT1</b>	<b>Central Treatment - Aerobic biological treatment</b>
<b>Pollutants</b>	BOD and biodegradable COD
<b>Description</b>	Waste water is contacted with a microbiological community under aerobic conditions. Biodegradable compounds are degraded.
<b>Availability</b>	High
<b>Operating performance</b>	<p>This is the most widely used technique for dealing with waste waters from the sector. It may be operated on site or after discharge to a water company's sewerage system</p> <p>Issues to consider when utilising the technique include:</p> <ul style="list-style-type: none"> <li>• inhibition - some compounds can inhibit the microbiological community and thus reduce removal effectiveness;</li> <li>• recalcitrant organics - certain compounds ('hard' COD) are non-biodegradable and will pass through untreated</li> <li>• nutrients - some waste waters may be deficient in the nutrients to support the microbiological community. Nutrient dosing will be required in this situation</li> </ul>
<b>Environmental impacts</b>	<p>A sludge is generated which will require disposal. This may be contaminated with metals and other non-biodegradable compounds</p> <p>Poorly operated treatment works may give rise to an odour problem.</p>
<b>Costs</b>	

<b>CT2</b>	<b>Central Treatment - Anaerobic biological treatment</b>
<b>Pollutants</b>	BOD and biodegradable COD
<b>Description</b>	Waste water is contacted with a microbiological community under anaerobic conditions. Biodegradable compounds are degraded.
<b>Availability</b>	High
<b>Operating performance</b>	<p>Anaerobic treatment will not tend to be used as frequently as aerobic treatment in this sector. Its use will be confined to situations where</p> <ul style="list-style-type: none"> <li>• the waste water is particularly strong (in terms of BOD???)</li> <li>• there are size constraints at a site (anaerobic systems tend to be smaller than aerobic);</li> <li>• specific compounds are more amenable to anaerobic rather than aerobic degradation.</li> </ul>
<b>Environmental impacts</b>	<p>A sludge is generated which will require disposal. This may be contaminated with metals and other non-biodegradable compounds</p> <p>Poorly operated treatment works may give rise to an odour problem.</p>
<b>Costs</b>	

<b>CT3</b>	<b>Central Treatment - Reed beds</b>
<b>Pollutants</b>	BOD
<b>Description</b>	The waste water is passed through an artificial reed bed. This supports a microbiological community which degrades biodegradable compounds
<b>Availability</b>	Medium
<b>Operating performance</b>	<p>Reed beds would be considered if:</p> <ul style="list-style-type: none"> <li>• there is plenty of space available;</li> <li>• the waste water contains predominantly organic/biodegradable compounds of a relatively low strength (&lt; 2000 mg BOD<sub>5</sub>/l);</li> <li>• there is a requirement for final 'polishing' of an effluent.</li> </ul>
<b>Environmental impacts</b>	The impacts are generally positive due to the creation of a new habitat for wildlife
<b>Costs</b>	Low

<b>CT4</b>	<b>Central Treatment - Chemical coagulation</b>
<b>Pollutants</b>	Metals and particulates
<b>Description</b>	Chemicals are dosed to and mixed with the waste water to enhance flocculation and precipitation
<b>Availability</b>	High
<b>Operating performance</b>	<p>A wide range of chemicals may be used in this manner</p> <p>The most commonly used chemical coagulants are aluminium sulphate, ferric sulphate and ferric chloride</p> <p>Chemical treatment will usually need to be followed by a separation stage to isolate the solid material from the waste water, for example sedimentation, flotation.</p> <p>pH adjustment may also be required to enhance the coagulation/flocculation.</p>
<b>Environmental impacts</b>	A sludge will be formed that will need to be removed for treatment and/or disposal
<b>Costs</b>	

<b>PT1</b>	<b>Polishing - Ozone</b>
<b>Pollutants</b>	Recalcitrant organics
<b>Description</b>	Waste water is contacted with ozone. The ozone is generated by passing dried air or oxygen between electrodes separated by a dielectric. The ozone oxidises organic compounds
<b>Availability</b>	High
<b>Operating performance</b>	<p>An oxygen rich environment poses a fire risk and suitable precautions should be taken</p> <p>Ozone is a non-selective oxidiser. Care should be taken to remove easily oxidisable materials from the waste water to ensure that the ozone is used to oxidise the recalcitrant compounds</p> <p>There are a wide variety of options for using ozone, these include:</p> <ul style="list-style-type: none"> <li>• ozone with ultra-violet (UV) radiation - improves removal efficiencies and broadens the range of compounds that can be dealt with. Turbidity results in poor transmission of UV through the waste water and reduces removal efficiencies;</li> <li>• ozone with UV and hydrogen peroxide. The peroxide enhances the creation of the hydroxyl radical and thus improves removal efficiencies. Ammonia will compete for the hydroxyl radical and so waste waters should be well nitrified prior to application of this technique. This is still a fairly novel technique and has not been widely applied;</li> <li>• ozone with adsorption. The target compounds are adsorbed onto a metal hydroxide and the resulting slurry is ozonated. The metal hydroxide improves removal efficiencies by catalysing the oxidation process. This is a novel technique and has yet to be widely demonstrated.</li> </ul>
<b>Environmental impacts</b>	<p>Dry air or oxygen should be used during the formation of the ozone, otherwise NO<sub>x</sub> may be formed</p> <p>Ozone can produce partial oxidation products which, whilst not toxic, can increase the BOD of the waste water.</p> <p>Residual ozone may require destruction. For example, using an oxidiser or activated carbon</p>
<b>Costs</b>	

<b>PT2</b>	<b>Polishing - Activated carbon</b>
<b>Pollutants</b>	Pesticides and other recalcitrant organics
<b>Description</b>	<p>The target compounds are adsorbed to the activated carbon. Two types of activated carbon are available:</p> <ul style="list-style-type: none"> <li>• granular activated carbon (GAC) is usually used in regenerable bed form;</li> <li>• powder activated carbon (PAC) is usually used in non-regenerable, powder form.</li> </ul>
<b>Availability</b>	High
<b>Operating performance</b>	<p>The effectiveness of GAC depends on the affinity of the target compounds for adsorption on GAC</p> <p>The effectiveness can be reduced when other organic compounds compete with the target pollutant for the finite number of adsorption points</p> <p>A system needs to be in place to detect when the adsorption capacity of the GAC has been utilised e.g concentration in the treated effluent</p> <p>Regeneration will usually be undertaken off-site by a specialist contractor</p> <p>PAC is superior to granular activated carbon (GAC) in terms of its specific capacity to adsorb organic compounds.</p> <p>Unlike GAC, PAC is usually only used once and must be disposed of as a sludge.</p> <p>PAC is probably better than GAC when the removal of organics is intermittent and thus it can be dosed to the waste water as and when necessary</p>
<b>Environmental impacts</b>	The GAC needs to be periodically regenerated or replaced both of which may give rise to environmental impacts
<b>Costs</b>	



<b>PT3</b>	<b>Polishing - Zeolites</b>
<b>Pollutants</b>	Metals and recalcitrant organics
<b>Description</b>	The waste water is passed through the zeolite which selectively adsorbs compounds of a certain size. The zeolite has a finite number of adsorption points and will have to be periodically regenerated
<b>Availability</b>	Medium
<b>Operating performance</b>	A wide range of zeolites are available to deal with compounds of many different sizes For complex waste waters some pre-treatment may be required to ensure that the zeolite does not preferentially adsorb the non-target pollutant
<b>Environmental impacts</b>	When the zeolite is regenerated, or disposed of, a waste stream will be generated that requires treatment
<b>Costs</b>	

<b>PT4</b>	<b>Polishing - Membrane Treatment</b>
<b>Pollutants</b>	Recalcitrant organics
<b>Description</b>	Waste water is passed through a barrier (membrane). Particulates and large dissolved molecules are retained behind the barrier leaving a clean effluent
<b>Availability</b>	High
<b>Operating performance</b>	<p>A wide range of membranes are available. These are largely differentiated by the size of particle/molecule that they retain. Examples include reverse osmosis, nanofiltration, ultrafiltration and microfiltration. Ceramic microfilters are being developed that form the membrane out of chemicals deposited onto a support matrix.</p> <p>An equally wide variety of materials are available for the manufacture of the membrane. These include polyamides, thin film composites and cellulose acetates.</p> <p>Some membrane materials may be damaged by halogens, such as chlorine, whilst other organic compounds may adsorb to the membrane, thus reducing its effective life</p>
<b>Environmental impacts</b>	The target pollutants are retained in a concentrated waste stream (approx 10% of the volume of the influent). This will need to be treated. In certain cases reuse/recycle may be possible
<b>Costs</b>	

## **APPENDIX B TECHNICAL DISCUSSION OF SECTORS**

### **B1. INTRODUCTION**

This appendix provides a technical discussion of the individual sectors of the chemical industry covered by the study. Section 2.2 of the report provides a discussion of the basic unit processes that are applied in all sectors. This appendix does not repeat that general discussion. Instead it concentrates on those issues that are specific to a sector. The main points discussed in this annex are summarised in Section 2.3.

The sectors covered by this appendix are:

- IPC Guidance Note IPR4/7 - Processes for the manufacture of organo-metallic compounds;
- IPR4/8 - Pesticide processes;
- IPR4/9 - Pharmaceutical processes;
- IPR4/12 - Processes for the sulphonation or nitration of organic compounds;
- IPR4/15 - Processes for the halogenation of organic chemicals.

### **B2. ORGANO METALLIC COMPOUNDS**

#### **B2.1 Introduction**

Organo-metallics contain a direct carbon-metal bond. A wide range of metals can form such bonds but the manufacture of organo-metallic compounds is based primarily on just three metals - lead, lithium and magnesium. A number of other organo-metallic compounds are produced on an industrial scale but these are not covered by the IPC system because:

- the only releases from the production of organo-silicons are of hydrogen chloride and therefore these compounds have been covered under hydrogen chloride processes;
- titanium, mercury and cadmium compounds manufactured in the UK contain a metal-oxygen bond and are therefore not truly organo-metallics;
- aluminium compounds are not manufactured in the UK; and

- a wide variety of other compounds (e.g based on gallium, indium and tellurium) are not produced in large enough quantities to warrant control under IPC.

Lead is used in the manufacture of lead alkyls which, despite the rapidly increased market share of lead-free fuel, is still used as an anti-knock agent in petrol. The main lithium based product, n-butyllithium, is used as an initiator for polymerisation processes, whilst magnesium is used to produce Grignard re-agents, important precursors in a wide range of chemical syntheses.

Whilst each of these three types of compound require unique approaches towards their production, there are also a number of issues common to them all. These include:

- strongly exothermic reactions, which if they go wrong can result in the need to vent the contents of reactors;
- the sensitivity of the reactions to the presence of atmospheric oxygen and moisture, which can compromise product quality and in certain cases can give rise to pyrophoric reactions;
- the use of large amounts of hydrocarbon based solvents to avoid moisture problems;
- the presence of both organic and metal based pollutants in wastestreams;
- the use of large stoichiometric excesses improves yields but increases raw material use and waste arisings;
- a large number of side reactions that can reduce reaction yields and increase the complexity of the waste produced.

In addition to these general issues, the production of each type of compound gives rise to a number of specific issues. These include:

### **B2.1.1 Manufacture of lead alkyls**

This category comprises the manufacture of tetraethyl and tetramethyl lead (TEL and TML). TEL and TML are currently produced by essentially the same process world-wide. This is the reaction of a lead/sodium alloy with ethyl- or methyl chloride batchwise to give TEL or TML respectively.

#### **Process description**

The alkyl chloride is added, at a controlled rate for TEL but as a whole charge for TML, to a batch reactor which has been pre-charged with lead/sodium alloy. The lead/sodium alloy is generally manufactured on the same site and transferred to the lead alkyl process in

transportable hoppers. The reaction produces lead alkyl and sodium chloride, as well as ethane and methane by-products. The reaction is carried out under pressure which is controlled to ensure that the volatile alkyl chloride does not flash off excessively at the desired reaction temperature. A reflux condenser is used to remove the heat of reaction.

On completion of the reaction, the reactor contents are purified by steam distillation. The lead alkyl is distilled off the reaction mass by live steam injection. The distillation top product is condensed and the lead alkyl/water mixture then undergoes a number of phase separations. Lead alkyls and water separate readily as they have a low mutual solubility and lead alkyls have a high specific gravity.

All blended products are purely physically mixed blends with one exception. In this chemical blend TEL and TML react in the presence of a boron trifluoride catalyst to produce a mixture of tetra, tri-mono, and di-alkyl lead species.

### **Releases into air**

There are numerous release sources from lead alkyl processes to atmosphere including:

- process vents;
- emergency relief vents;
- collection pit vents;
- blending and bulk storage facilities' vents; and
- general building extract ventilation.

The type and degree of release control applied can vary depending on the significance of the release source.

Where appropriate gaseous streams containing TEL are often treated by absorption of the lead alkyl into mineral oil in a packed tower. TEL is then recovered from the oil by stripping under vacuum and heat. This can be a less efficient process than carbon adsorption but does not have the same decomposition problems. Other possible treatment techniques include incineration and reduction of lead alkyls by contacting with lead dioxide.

Gaseous off-gas streams containing TML can be treated by carbon adsorption, which is a relatively high efficiency process, typically 90% of total TML can be removed.

Process vents from the reaction and distillation stages often pass through a condensation and/or compression system before discharge to atmosphere. This enables significant quantities of alkyl chloride (excess is used during the reaction stage to provide cooling by reflux) to be recovered and recycled directly for use as a raw material.

## **Releases into water**

All liquid/sludge wastes from lead alkyls manufacture drain into an enclosed collection pit. This pit is maintained under slight vacuum and the vent exhaust, which will contain significant levels of lead alkyl vapour, is treated before discharge to atmosphere. Liquid is pumped from the collection pit to an effluent treatment plant. Solids and sludge settle in the bottom of the pit from where they are removed, dried and fed to a lead recovery furnace. The recovery of lead metal from the collection pit sludge is outside the scope of this study.

When both TEL and TML are manufactured on the same site, it is usually necessary to segregate the treatment of the effluent streams, i.e. separate collection pits for the two compounds.

Liquid effluent streams from the collection pits usually require a number of treatment stages to satisfactorily minimise the pollutant load of the effluent discharge. Streams from a lead alkyl process require pH control to minimise the solubility of any inorganic lead compounds and to meet any pH consent limit. The original stream is alkaline because the sodium from the lead/sodium alloy reacts with water to form sodium hydroxide in the distillation stage. The effluent also passes through settling tanks where carryover of solids, sludge or TEL settle out and are recycled back to the lead recovery process, or treated further to recover lead alkyl product. In the latter case solids can still be separated and sent for lead recovery. The final effluent is then discharged from site.

A treatment stage is generally also required to minimise the soluble organic lead content of the effluent. The soluble organic lead content mainly comprises ionic trialkyl lead species which are formed by the partial decomposition of tetra-alkyl lead compounds in water. Possible abatement techniques include reduction of soluble lead alkyls with either sodium borohydride or an active metal, such as zinc, chemical precipitation followed by adsorption and ozone treatment. Treatment with sodium borohydride or an active metal are most commonly employed.

## **Releases to land**

- sludges from the liquid effluent treatment processes;
- slag from lead recovery furnaces;
- spent oil from the TEL absorbers;
- spent carbon from the TML carbon adsorbers.
- scrapped drums, other process equipment and pipework together with protective clothing.

### **B2.1.2 Manufacture of lithium alkyls**

Compounds manufactured in this category are n-, sec- and tert-butyllithium. Commercial manufacture of butyl-lithium world-wide is carried out by the same process, i.e. the direct reaction of lithium metal with a butyl halide in a hydrocarbon solvent.

Lithium metal is heated and dispersed in a mineral oil. This mixture is then transferred to a cooling vessel where the lithium dispersion solidifies as a finely divided shot. The lithium shot is washed with a hydrocarbon solvent (typically hexane, cyclohexane or isopentane).

The cleaned lithium shot/solvent mixture is transferred into a batch reactor. Butyl chloride is added at a controlled rate and the reaction, which is exothermic, produces butyllithium and some lithium chloride by-product. Excess lithium is used to ensure complete consumption of the butyl chloride.

The reactor contents are filtered and the filtrate, i.e. butyl-lithium product in hydrocarbon solvent, is transferred to product storage. The residues which comprise lithium metal, lithium chloride and solvent, are transferred to a water filled quench tank to convert the "excess" lithium metal to lithium hydroxide. Hydrochloric acid is added to produce lithium chloride. The mixture is then allowed to settle. The bottom layer of lithium chloride solution can be returned to an inorganic lithium process for recovery of the lithium metal. Argon is normally used as the inerting gas during the formation of lithium shot. A nitride film is formed if nitrogen is used.

Depending upon customer requirements, butyl-lithium is blended with the same solvent used for the reaction, e.g. hexane, cyclohexane or isopentane, to give solutions between 12 - 24% w/w butyllithium. Butyl-lithium at 24% w/w is generally considered pyrophoric under all ambient conditions likely to be encountered.

#### **Releases into air**

As the process is operated at ambient temperature and pressure only the butyl chlorides and hydrocarbon solvents have significant vapour pressures. Losses are therefore incurred by displacement venting from bulk and finished product storage vessels. Butyl-lithium compounds are fairly involatile.

Venting of inert gas atmospheres from all process stages up to quenching of the filter cake slurry. These will include butenes and octenes from the butyl-lithium reactor.

#### **Releases into water**

The liquid effluent discharged to drain from lithium alkyls processes is limited. Mineral oil and hydrocarbon solvent wastes are either transferred to on-site recovery processes or

sent for off-site recovery or disposal. The main aqueous process waste is lithium chloride brine which is sent for lithium metal recovery.

### **Releases to land**

Solid waste arising from filtration contains trace contamination of inorganic lithium salts, solvent and mineral oils.

The top layer solvent is generally unsuitable for re-use because of the impurities it contains and so is sent for off-site disposal.

### **B2.1.3 Grignard reagents**

Grignard reagents are organo-magnesium halides. The most commonly used are alkyls, generally methyl or ethyl groups. Similarly, the halide used is usually a chlorine or bromine. The use of Grignard reagents is a classical synthesis route for many organic chemicals.

Grignard reagents are manufactured commercially as intermediates in a multi-stage synthesis. They are generally not a final product but are completely consumed by the process. The majority of Grignard reagent manufacture is carried out batchwise by the addition of an organo-halide to magnesium turnings in another solvent.

The most common preparation of Grignard reagents is the batch reaction of an alkyl halide with magnesium turnings in an ether solvent. The ether solvent and magnesium metal are charged to a batch reactor. The alkyl halide is added at a controlled rate and the resulting reaction produces the alkyl magnesium halide, i.e. Grignard reagent. A slight excess of magnesium is usually used to ensure complete consumption of the alkyl halide. The reaction is highly exothermic and the heat of reaction is generally removed by reactor cooling and/or use of an overhead reflux condenser.

Grignard reagents are rarely the final product. The next stage therefore is generally the addition of a second reactant. The ensuing reaction adds the alkyl group from the Grignard reagent to the second reactant, leaving a magnesium halide and the desired product.

In some instances water is added because a hydrolysis reaction is required to complete the formation of the desired product.

The reaction batch is generally distilled to recover the ether solvent for re-use. In processes where water has previously been added, the distillate collected will be an ether/water mixture which will require further treatment to reduce the water content of the ether sufficiently that it is suitable for re-use. It should be noted that in some processes the distillation precedes the hydrolysis stage.



The final stage of the process is generally acidification. A small amount of an acid, usually sulphuric or hydrochloric, is added to ensure that any residual magnesium metal is reacted, as well as any insoluble magnesium hydroxide complexes that may have formed. The mixture is allowed to settle and separates into an aqueous and an organic phase.

The organic layer is the desired product and is run off to final product storage or further processing stages, as appropriate. It should be noted that this organic product is usually not an organo-metallic compound. The purpose of the Grignard reagent is to donate an organic radical to the second reactant. All the magnesium is converted to inorganic magnesium salts in the aqueous layer, along with some excess acid and possibly some ether solvent. This aqueous layer is run-off to the site effluent drainage system.

The process above is carried out under an inert atmosphere, usually nitrogen. The main reasons for this include:

- ethers can react with oxygen to form explosive peroxide compounds;
- alkyl halides can form explosive mixtures with air; and
- exclusion of atmospheric moisture from the process.

The presence of water at the start of the process will inhibit the formation of the Grignard reagent. Once formed, Grignard reagents decompose violently in the presence of water. For these reasons, the water content of the raw materials, particularly any recovered ether solvent, is minimised; also, cooling coils and overhead condensers often use a non-aqueous coolant.

Other processes exist for the continuous formation of Grignard reagents. One involves passing an organohalide/ether solution through a column packed with magnesium particles. This technique is generally used for those Grignard reagents which are difficult to produce in a batch process due to unwanted side reactions.

Another process involves the continuous production of Grignard reagents in several agitated batch reactors which then overflow to a holding tank from which the Grignard reagent is continuously removed. This process was developed specifically for a process to manufacture lead alkyls on a continuous basis by electrolysis of a Grignard reagent using a lead anode. Lead alkyls are no longer manufactured commercially using this technology.

### **Releases into air**

Ether solvent, alkyl halide and gaseous reaction by-products are released from:

- displacement venting and blowthrough from pressurised transfer vessel;
- venting of vessel inert atmospheres;
- ether reflux and distillation stages.

### **Releases into water**

The aqueous layer from the organic/aqueous phase separation stage runs to drain and consists of: ether, water soluble magnesium salts and acid.

It is important to ensure that the organic product is not discharged along with the aqueous waste if the product compounds could cause significant harm to the aqueous environment.

### **Releases to land**

There is little or no solid waste except for decontaminated raw material drums.

#### **B2.1.4 Small volume organo-metallic compound manufacture**

This category covers a very wide range of organo-metallic compounds, manufactured in small quantities, typically 1-100 kg year<sup>-1</sup>. A small number of these processes may manufacture up to several tonnes a year of product, e.g. dibutyl-magnesium. Most of these products are produced for research and development applications although there are a number of genuine commercial applications for some small volume organo-metallic compounds. However, the toxic nature of some of the compounds involved means that the potential impact of the manufacturing processes may be significant despite their low volume.

A wide variety of processes are used including those types of reactions discussed in previous sections, e.g. direct metal alkylation using an alkyl halide or a Grignard reagent. Typically, the process stages will be similar to those in the large scale manufacturing processes, e.g. batch reaction, distillation and filtration. However, most of these processes will be carried out in glass laboratory equipment. A few of the higher volume products are manufactured in "pilot plant" scale equipment.

### **Releases into air**

Purging of the nitrogen blanket, containing raw material, product or solvent. The quantities will depend upon the volatility of the materials and the operating conditions, as well as any abatement equipment installed.

Some gaseous organic compounds are produced as by-products. Without abatement equipment these will be released into the environment.

### **Releases into water**

In small volume organo-metallic compound manufacture, as for large scale, the absolute quantities of liquid and/or solid effluent produced are usually significantly greater than the quantities of gaseous effluent. In some cases this is accentuated by a high purity

specification; a much higher percentage of product is discarded in the liquid or solid effluent. This may include solid complexes generated by the addition of isopropanol.

### **Releases to land**

Because manufacturing sites of this type typically produce a large number of diverse products, in small quantities at irregular intervals, on-site liquid and solid effluent treatment may not be practicable. This waste is therefore generally stored on-site and sent for off-site treatment or disposal.

Spent activated carbon, and contaminated filter aid is also produced.

## **B3. PESTICIDES**

### **B3.1 Introduction**

The Pesticide processes description covers the manufacture or formulation of insecticides, fungicides, herbicides, plant growth regulators and other chemicals for controlling pests and diseases in agriculture, horticulture, forestry and aquatic herbicides, preservatives, mothproofing chemicals, rodenticides and food storage pesticides.

Primary pesticide manufacturing conventionally entails synthetic organic chemistry generally using several process steps to build up an active chemical entity from simple raw materials or specific chemical intermediates. Secondary processing involves the formulation of the pesticide in a marketable form. The unit processes used in primary pesticide manufacture will be very similar to those described generally in Section 2.2.

Typically manufacture and formulation are both discontinuous batch processes, the timing and duration of each campaign depending on the seasonal needs of the markets served. In general, multi-purpose plant is used for formulation of many different products.

### **B3.2 Interaction with other regulatory systems**

As with the manufacture of pharmaceuticals there is a need to obtain prior approval to supply pesticides. The Food and Environmental Protection Act 1985 provides the framework for the control of the supply of pesticides, the Control of Pesticides Regulations 1985 outline in detail the prior approval system and the Pesticides Safety Directorate (PSD), an agency of the Ministry of Agriculture, Fisheries and Food (MAFF), operates the system. Although perhaps not quite as draconian as the controls on the supply of pharmaceuticals, this prior approval system for pesticides is an important potential constraint on any proposed changes to the process.

### **B3.3 Types of pesticides**

A wide range of products are marketed under the general descriptor of pesticide. These include:

- insecticides, which are used against insects. The most commonly found of which are based on:
  - organochlorines;
  - organophosphorus compounds;
  - carbamates;
  - pyrethrin and synthetic pyrethroids.
- herbicides, which are used against plants. The most commonly found of which are based on:
  - phenoxyaliphatic acids e.g 2,4-D;
  - substituted ureas e.g diuron;
  - nitroanilines e.g trifluralin;
  - hetrocyclic nitrogens e.g simazine and atrazine.
- fungicides, which are used against fungal infections;
- Rodenticides, which are used against animals; and
- biological agents, which may be used against insects, plants and fungal growths.

### **B3.4 Primary pesticide manufacture**

Primary pesticide manufacture generally utilises the unit processes discussed in Section 2.2. The most important issue unique to the primary manufacture of pesticides is the toxicity of the raw materials, products and wastes. These may justify a higher level of control during all unit process stages and may also require attention if biological based abatement techniques are to be used.

#### **B3.4.1 Receipt of raw materials**

The basic considerations that underpin the supply of raw materials are similar to those described in section 2.2. Additional considerations include:

- active ingredients for pesticide formulation are often imported in relatively small quantities and the UK recipient currently has little, but increasing, control over the type of packaging used;

- dry active ingredients and additives are most commonly supplied in 25 kg, polyethylene-lined paper sacks or fibreboard kegs, although larger (0.5-1 tonne) fibre bags, or bulk delivery from tanker may be available;
- liquid active ingredients, solvents and additives are usually supplied in steel drums, often polypropylene lined, or in polypropylene drums. For larger scale operations bulk delivery from tanker may be available;
- in some cases, where active ingredients are formulated on the manufacturing site, they may be piped directly to the formulation plant, often via intermediate holding vessels;
- solid residues may include: packaging materials, i.e. steel drums, polypropylene-lined steel drums, polyethylene lined paper sacks and fibreboard kegs; protective clothing; used air filters; spent carbon filters; solid wastes recovered during treatment of liquid effluent; shake-down dusts from filters; vessel scrapings; and off-specification product.

#### **B3.4.2 Materials storage**

Dry ingredients and finished products are usually stored in bunded warehouses prior to use. Liquid ingredients are stored in external bunded areas, in the bunded warehouse or in bunded bulk storage tanks. The general issues relating to storage that are discussed in Section 2.2 will apply to storage, although the hazardous nature of many of the materials used in the manufacture of pesticides may require their particularly stringent application.

#### **B3.4.3 Vessel charging**

##### **Dry ingredients**

The main issues to consider are:

- in most cases the smaller containers are manually opened or split, inverted over a charge hopper or mixing vessel, and the contents are shaken out. The packaging material is compacted and overwrapped for disposal. Dust escape is reduced by use of local laminar flow extraction systems;
- for large scale operations, semi-automatic sack splitting equipment is sometimes used. The sack is loaded unopened into the equipment and then automatically split and shaken out, removed, compacted and overpacked, all under negative pressure;

- large bags can often be connected directly to a weigh feeder which is vented to a dust collector. The weigh feeder delivers the correct amount of material to the formulating tank; the connection can then be closed and the bag disconnected;
- bulk supplies from tanker, storage silos or direct from the manufacturing plant can be piped directly into the formulation vessel via weigh feeders;
- dusts may result from: vessel charging with dry active ingredients; drying and cooling operations; the conveyance of granules; packing of powders and granules; mixing of dry ingredients; packing and compacting of used packaging materials; plant clean-down; and fugitive releases from seals, valves etc.

## **Liquids**

The main issues to consider are:

- drums are usually opened manually and the contents should generally be pumped into the formulation vessel;
- the emptying of viscous liquids is usually enhanced by warming the drums in a hot water bath or warm room;
- liquids from tankers, storage tanks or manufacturing plant are piped into the formulation vessel;
- emissions of VOCs may result from the charging of vessels with volatile liquids.

### **B3.4.4 Secondary pesticide manufacture (Formulation)**

Formulation normally only involves physical operations such as vessel charging, mixing, milling, warming, cooling, product transfers, granulation, drying, sieving and packing. No chemical reactions take place.

Pesticides are formulated in a number of different forms, for example, emulsifiable concentrates, oil in water emulsions, flowable concentrates, granules, water dispersible granules and wettable powders, depending on the characteristics of the active ingredient itself and the demands of the market served. Typically the formulation processes involve the following steps:

#### **Receipt of raw materials, storage and vessel charging**

See above.

### **Liquid pesticide formulation**

A typical process involving the manufacture of a liquid pesticide formulation may involve the following steps:

- mixing of pesticide concentrate, with solvent (e.g light aromatics such as xylene, chlorinated organics such as 1,1,1 trichloroethane and mineral spirits. Selected solvents are usually of low volatility) and any inert materials (e.g wetting and dispersing agents, masking agents, deodorants and emulsifiers) associated with the formulation;
- filtration to separate solids from the target (liquid) compound;
- packaging; and
- container testing.

### **Solid pesticide formulation**

A typical process involving the manufacture of a solid pesticide formulation may involve the following steps:

- crushing and/or pulverising of the pesticide active ingredient;
- blending with a carrier agent;
- high speed grinding;
- blending with additives;
- fluid energy mill;
- blending with additives;
- packaging.

All of which may give rise to releases of particulates.

### **Packaging**

Pesticide products are generally packed on standard liquid, powder or granule packaging lines at the formulation plant. Those parts of the line where product filling takes place, or where containers are conveyed uncapped, are partially enclosed and fitted with local extraction systems for collection of dust and volatiles. Generally, liquids are packed into 1 or 5 litre plastic containers. Solids are usually gravity fed from hoppers into sachets or boxes.

## **Clean-down operations**

Routine clean-down is generally carried out on a daily basis. Spillages should be cleaned immediately if they occur. At the end of a formulation campaign major clean-down of facilities and equipment takes place in order to avoid cross contamination of products.

# **B4. PHARMACEUTICALS**

## **B4.1 Introduction**

Of the sectors of the chemical industry covered by this study, the pharmaceutical sector is the one that deviates most from the basic unit process approach outlined in Section 2.2. This section outlines the unit processes that by and large will not be found in the other chemical sectors covered by this study but which are extensively used in the manufacture of pharmaceuticals.

There are two key factors to consider when discussing pollution prevention and control in the pharmaceutical industry. The first is the interaction between the different regulatory systems for pharmaceutical product approval and environmental protection, administered by the Medicines Inspectorate and the Environment Agency, respectively. The second is the high purity/quality requirements associated with the industry. Both of these factors can limit the opportunities for reducing the environmental impact of existing processes and so perhaps more than any other sector, pharmaceuticals lends itself to 'designing' the environment into new processes/products at a very early stage.

Pharmaceutical manufacture is divided into two major stages. The first stage, which is typically referred to as primary processing or manufacture, is the production of the active ingredient or drug. The second stage, secondary processing, is the conversion of the active drugs into products suitable for administration or use. It generally involves the physical formulation, filling and packaging of the final pharmaceutical product in the correct dosage form. Formulation is the combination of the active ingredient with other appropriate chemicals in the preparation of the final dosage form. Formulation may be alternatively referred to as galenical production.

## **B4.2 Pharmaceutical products**

Pharmaceutical products are intended for veterinary and medical use, and can be classified into three main groups:



- proprietary ethical products or prescription only medicines (POM). These patented products are supplied under a manufacturer's trademark and are obtained by the general public on prescription from a medical practitioner;
- generic ethical products. These are standard prescription only medicines made to a recognised formula, which may be specified in standard reference books, and may be manufactured by a number of different companies;
- over-the-counter (OTC) or non-prescription products. These products are available direct to the public.

The products of secondary pharmaceutical manufacture are available in several forms:

- tablets;
- capsules;
- liquids, which may be in the form of solutions, suspensions, emulsions, gels or injectables;
- creams and ointments, which usually consist of an oil in water emulsion (cream) or a water in oil emulsion (ointment);
- aerosols, which contain inhalable products or products suitable for external use. Propellants have conventionally been chloro-fluorocarbons (CFCs). More recently butane has been used in externally applied products.

### **B4.3 Other regulatory constraints on pharmaceutical manufacture**

The manufacture of pharmaceutical products in the United Kingdom is controlled by Good Manufacturing Practice (GMP) regulations and is regulated by the UK Medicines Inspectorate. Additionally, if products are exported to the United States or Japan, the product and manufacturing processes will be subject to US and Japanese regulations and procedures, including site inspections.

Changes to manufacturing processes and raw materials must be approved by the regulatory authorities prior to implementation, and this is not easily achieved. Traditionally, licences to market pharmaceuticals required the manufacturer to use the same production process/raw materials for the lifetime of the product. Thus relatively recent concerns about health, safety and the environment have required the manufacturer to initiate an often time consuming and costly re-approval procedure. The fitting of new abatement equipment, changing from chlorinated solvents to aqueous based systems etc. would all require re-approval in this manner.

For existing processes these changes are likely to be required as process operators introduce best practice and respond to changes in BATNEEC. However, for new

processes a degree of 'future proofing' should be possible by ensuring that environmental protection is designed in from the beginning of processes/product development and that the techniques applied are likely to be the 'best' for many years to come.

The USA now requires (post April 1985) that all New Drug Approval (NDA) applications must be submitted with an environmental assessment report addressing the fate and toxicity of drugs and their metabolized by-products. An important implication of these Environmental Assessment requirements is that they apply world-wide to all facilities inspected by the Food and Drug Administration (FDA), and to all drug re-registration applications. With each NDA application, the applicant is required to provide comprehensive data on estimated production figures and on waste generation. The environmental assessment data relates to the parent drug, not all metabolites, and includes:

- physical and chemical properties;
- biodegradability;
- photolysis propensity;
- aqueous toxicity (fish);
- prediction of capability of existing treatment plant to treat waste;
- treatment sequences that are capable of treating the wastes.

If the environmental assessment shows no significant effects, a finding of no significant impact (FONSI) is declared. If there are potential adverse environmental effects, a full environmental impact statement (EIS) is required, with a public hearing. An interim guide for environmental assessment compliance requirements for the FDA was prepared for the Pharmaceutical Industry jointly by the FDA and the USA Pharmaceutical Manufacturers Association in July 1991.

These environmental assessment requirements are still predominantly driven by concerns about the environmental impact of using the pharmaceutical product rather than manufacturing it. However, inspectors may wish to consider accessing the information provided by process operators to the pharmaceutical regulatory authorities when it may help them consider an application.

#### **B4.4 Manufacturing programmes**

Drugs are manufactured in 'campaigns', in which one or more process units are used solely for the manufacture of a single product for a period of time. Campaigns involve tightly scheduled and detailed co-ordinated activities. They may comprise a series of identical production batches. The products are manufactured in a series of steps according to a definite recipe. Operations are controlled either manually or, increasingly more so, by computer. Continuous and semi-continuous operations may also be carried out, but are far less common than batch processing. Products manufactured in substantial amounts may be made in dedicated plant designed for one process sequence.

Pharmaceutical processing is primarily of a batch nature; where this is the case, the equipment should be versatile, easy to clean, and capable of being used to produce more than one product.

## **B4.5 Manufacturing facilities**

### **B4.5.1 Containment**

Facilities should preferably be designed to prevent contact of product with operating personnel and the environment. This containment strategy has a dual objective: the prevention of product contamination and cross-contamination; and the protection of the operator and the environment. Containment is used for systems which handle dry and liquid materials in batches, and has been developed largely within the Pharmaceutical Industry. Containment is an important means of minimising fugitive releases - the concept can be applied to facility design, as well as to the design of equipment, storage and transfer systems. For existing plants the extent to which containment is practised varies from site to site and depends to a large extent on the age of the facility. Since this concept is relatively new, only recently built or modified plants will incorporate total containment processing.

### **B4.5.2 Island systems**

Secondary production facilities will consist typically of a series of discrete modules which should be integrated in such a way as to minimise material flow requirements and which concentrates areas of the same cleanliness class. This is known as the 'island' system. Thus critical areas will be maintained within small, closed zones and segregated from areas of potential contamination by means of air locks. The non-critical zones and service areas should be physically detached and contain all the motors, ventilation and power systems. Contamination of the process area by heat radiation, noise and exhaust will therefore be minimised. All equipment washing water should be collected, contained, and piped into the service area.

### **B4.5.3 Cleanliness**

The buildings should be designed to be easily maintained, cleanable and to have low bio-burden and dirt-retention properties. The finishes should also reflect GMP-compatible requirements i.e.:

- typically ceilings should be jointless and suspended;
- flooring materials should be carefully selected; terrazzo tiles are common flooring finishes in the UK, but require grouting;

- walls should be smooth for easy cleaning, and non-absorptive; polymeric finishes are suitable;
- stainless steel or PVC finishes on doors and windows should be used;
- joins to the wall at floor and ceiling level should be covered and sealed;
- there should generally be no drains where pollutants and microbes may accumulate. All floors in secondary production areas should be cleaned, with the minimum of water, with a mop and bucket. Consequently accidental spills can not be flushed undetected into the sewer system.

#### **B4.5.4 Storage**

Warehousing and storage facility design is an important aspect of pollution prevention in the Pharmaceutical Industry. Because of the often toxic and hazardous nature of substances commonly used in pharmaceutical production, secure and well-designed storage facilities are essential. Modern warehousing facilities may be computer-controlled and use automatically guided vehicles, overhead monorails or electrically-operated forklifts and trucks. Companies should pay attention to the protection of warehousing and storage facilities, so that in the event of a spill or fire, no chemicals will enter the water systems.

#### **B4.5.5 Process equipment**

New processes should preferably use contained equipment with a reduction of chemical-handling requirements. Features which are typical of this approach are as follows:

- the interconnection of equipment with a closely-coupled arrangement of ducts and flexible connections, which allows for contained transfer, dosing and weighing;
- the dual purpose use of standard stainless steel containers, which are designed to allow operations such as feeding, blending, granulating, milling, and sieving to start and end in the same container. These containers are also suitable for storage and transport. This procedure greatly reduces the risk of batch contamination, ensures batch integrity and minimises washing requirements, thus reducing the chance of waste water contamination;
- the use of multi-processing equipment, where a selection of operations is carried out in one vessel. Examples include granulator-driers and mixer-granulators for solid forms, and vacuum homogenisers for liquid forms;

- the physical encapsulation of equipment parts or pieces. Despite the high standard of mechanised and automated process machinery employed in the production of pharmaceutical products, there are still certain steps which require open manual handling. The encapsulation of the equipment in a control cabin allows for: contamination prevention; operator protection; dust separation; environmental protection; and economic operation.

#### **B4.5.6 The control of the internal environment :**

Control systems should ensure that all dust and organic vapours are removed from the process area. These systems consist of a capture device to collect pollutants and direct them to a control or treatment device, which ensures that pollution to the external environment is prevented or minimised. Capture systems may be local ventilation, partial enclosures or total enclosures. Extraction may be from a cubicle or from a piece of processing equipment.

Dust removal systems in the Pharmaceutical Industry tend to be of two types:

- dedicated dust collectors which are designed to control isolated waste streams from one or a selection of pieces of equipment;
- central dust collectors, which consist typically of a series of baghouse filtration systems, to which waste air streams are ducted from various locations within the processing area.

The design of an extraction system is critical when further treatment of this waste air, or recovery of contaminants from it, is required. Treatment and recovery systems for organic solvents are most effective when the waste stream is concentrated and of low volume.

#### **B4.5.7 Solvent use and recycling :**

Use of the correct solvent is critical in the manufacture of pharmaceuticals. A number of important issues should be considered when considering the environmental impact of solvent use in the industry. These include:

- recycling may be difficult because of:
  - high purity requirements;
  - the limited opportunities available for reusing a solvent in other parts of the process because of cross contamination concerns;
  - the conditions of marketing licences issued by the pharmaceutical regulatory bodies;
  - the difficulties of selling the recovered solvent into an external market when there is the risk, however slight, of contamination by the active ingredient.

- the industry has taken steps to reduce the amount of organic, particularly chlorinated, solvents that it uses. Aqueous systems are now widely used instead and not only reduce potential environmental impacts but also those associated with the risk of fire/explosion. However, aqueous systems may not be appropriate in every case, for example they may react with the active ingredient and they also tend to require more energy to dry and move;
- in the longer term super critical carbon dioxide systems may allow the replacement of both organic and aqueous solvent systems. This will probably lead to reductions in waste arisings and improved product yields but has not yet been demonstrated widely in the industry;
- certain equipment used in the manufacture of secondary pharmaceuticals give rise to large arisings of VOCs, in particular driers and coaters. New equipment can now be purchased that has an integral solvent recovery system.

## **B4.6 Primary manufacturing operations**

Primary pharmaceutical manufacture will typically involve several of the following steps:

- raw materials handling;
- storage;
- reaction;
- separation;
  - extraction;
  - decanting;
  - centrifugation;
  - filtration;
  - crystallisation.
- natural and biological product extraction;
- fermentation;
  - seed preparation;
  - fermentation;
  - product recovery.
- drying.

Each of these steps is discussed in more detail below if it is not adequately covered by Section 2.2 on the basic unit processes used in the chemical industry.

### **B4.6.1 Receipt of raw materials**

Raw materials are delivered in tankers, bags, drums, boxes or similar containers. The management of raw materials at a secondary pharmaceutical site should be underpinned by

the same basic procedures as are outlined in Section 2.2. Additional considerations, particular to this sector include:

- the use of special, high integrity containers to prevent contamination of raw materials prior to use;
- where pallets are used for delivery, the practice is to exchange the external pallet (often wood) for an internal pallet (steel or aluminium) to avoid contamination;
- raw materials will be analyzed on receipt for the presence of harmful contaminants. This requirement is likely to be defined by the pharmaceutical regulatory authorities;
- the identity of the chemical should also be checked to ensure that the correct chemical and purity is being used;
- raw materials consignments are likely to be bar coded on receipt.

The main environmental impacts associated with raw material receipt are from accidental releases, spillages etc.

#### **B4.6.2 Storage**

Storage at a secondary pharmaceutical site is likely to be underpinned by the same basic considerations as are outlined in Section 2.2. Additional considerations include:

- all materials entering the stores should be suitably labelled and/or coded to enable them to be traced to source;
- most large companies operate computerized stock control. Some warehouses are now completely automated;
- before containers are moved into the processing area the external surfaces are cleaned;
- whilst manual methods of handling have predominated in the past, recently there has been increased application of pneumatic conveying, and a few companies have now installed automated handling operations;
- appropriate precautions are usually taken to prevent the release to the environment of liquids (including fire fighting effluent) and solids in the event of a fire or spillage.

### **B4.6.3 Reaction**

The reaction vessels used in the pharmaceuticals sector are broadly similar to those used in the wider chemical industry. There is a trend towards the use of smaller reactors that offer greater flexibility.

### **B4.6.4 Separation**

The primary pharmaceutical sector makes extensive use of separation techniques. Many of these are widely applied elsewhere in the chemical industry and are discussed in Section 2.2. This section therefore confines itself to a discussion of crystallisation, a separation technique not widely applied elsewhere in the chemical industry.

Crystallisation involves the creation of a supersaturated solution in which crystals of the target compound are formed. There are three main alternatives for the creation of the supersaturated solution:

- cooling can be used if the solubility of the target compound in the solvent increases with temperature increases;
- evaporation can be used if the target compound's solubility is not temperature dependent or decreases with temperature increases;
- induced crystallisation caused by the addition of a further solvent, that results in the solubility of the target compound being reduced in the mix of the original and added solvent.

Compared to the other two techniques evaporation may cause significant arisings of VOCs emissions to air, although if recycling is feasible the impact of these emissions may be reduced.

### **B4.6.5 Natural product extraction**

Natural product extraction involves the isolation of an active ingredient from natural sources such as plants, roots etc. Because the active ingredient is usually only naturally present in very low concentrations natural separation often consists of a number of repeated concentration steps, each of which have the potential to give rise to large amounts of waste.

The basic steps involved in the process are:

- mixing and washing;
- extraction;
- evaporation.



Solvents are often used to remove fats and oils without damaging the essential active ingredient. Ammonia may be used during the extraction step as a method of controlling the pH when extracting from animal and plant sources. Ammonium salts are also used as buffering chemicals and aqueous or anhydrous ammonia is used as an alkalising agent. The high degree of solubility of ammonium salts prevents unwanted precipitation, whilst ammonium salts have the advantage of not reacting with animal and/or plant tissues.

#### **B4.6.6 Fermentation**

Fermentation involves the inoculation of micro-organisms (bacteria, yeast, fungi etc.) in a liquid broth in the presence of nutrients. The micro-organisms produce the desired product as a by-product of normal metabolism.

The main steps involved in fermentation are:

- seed preparation. This involves the introduction of the microbial strain to a primary seed fermentation, which is commonly performed using shaking-flask culture techniques at the laboratory scale. This stage may be repeated a number of times to produce enough inoculum for the production fermentor;
- fermentation. The inoculum produced during seed preparation is charged to a sterilized fermentor, where it is agitated and aerated. The resulting broth, which may take anything from a few hours to several weeks to form, is then filtered or centrifuged to separate out the solids; and
- product recovery. Filtration/centrifugation removes any larger residue from the broth but does not isolate the active ingredient. This can be achieved by three routes:
  - solvent extraction - a wide variety of solvents may be used to preferentially solubilise the target compound. Crystallisation, for example, can then be used to remove the solvent;
  - direct precipitation - this involves the precipitation of the product as a metal salt by the use of, for example, copper or zinc precipitating agents. The broth is then filtered and the target compound recovered from the solid filter residues;
  - ion exchange - an ion exchange, or activated carbon, column is contacted with the broth and the product adsorbs onto the resin. The product can then be recovered from the column by washing followed by crystallisation.

Occasionally the active ingredient may be contained within the cell walls of the micro-organism. In such situations cell wall breakage by heat or ultrasound, for example, may be required.

#### B4.6.7 Drying

Drying may be used at a number of points during the primary and secondary manufacturing of pharmaceuticals. It is often used as the final step in primary manufacture to evaporate off the remaining solvent.

Most drying operations use conventional equipment. Tray ovens, fluidized beds, vacuum driers, tumble driers, spray driers and freeze driers are commonly used in the Industry. Infrared and microwave drying are techniques which offer improved heat transfer. The drying time depends on the equipment and formulation, but may range from minutes to hours. Driers are potential sources of large volumes of releases. The main issues associated with driers are:

- release rates vary during the drying cycle, being greatest at the beginning of the cycle;
- releases vary with drier size, and the amount and type of solvent used;
- special precautions are taken during drying to ensure that the solvent concentration within the drier and associated equipment is maintained at a level outside the explosive range for the materials present. This frequently requires dilution of the air stream which makes organic release control more difficult;
- where there is a risk of explosion, driers should be located in the building in a position which should minimise the adverse consequences of explosions. There may be a need to allow explosion relief directly to atmosphere, which would permit the release of pollutants. (However, correct equipment design should limit the occurrence of ignition). Where these releases are unusually frequent, steps should be taken to modify the equipment to reduce the frequency of over pressure;
- waste air streams from driers should be extracted to abatement equipment which includes filters, cyclones or scrubbers. Other technologies such as condensation and oxidation may be used in specific cases. The choice of technique depends on the nature and concentration of the waste air, and the time required to process each batch.

The main types of drier are:

- **tray driers** rely on conventional heat transfer. Air is continuously circulated within a chamber containing a series of support racks. Tray driers are widely used in existing processes in the UK Pharmaceutical Industry despite their old technology. Their use continues mainly because of the expense involved in changing to alternative technologies. Tray driers are relatively inefficient in their drying operation compared with newer drying methods; typical drying times can be up to 48 hours. They create explosive, handling, dust and vapour problems.

Modern tray drier designs can, however, reduce many of the environmental problems associated with older designs;

- **fluidized-bed driers** are the most common type of drier currently in use in the UK Pharmaceutical Industry. Drying times are relatively short (1 to 2 hours) because of the efficiency of heat transfer. A major disadvantage of these systems is that significant amounts of energy and air are required to lift the bed and dry the product. This large amount of air has environmental consequences in cases where potentially harmful substances may be emitted; adequate control and treatment of waste air is difficult when the air is present in large volumes and contains a low concentration of pollutants. A further disadvantage of the method is the length of ducting that is required for the hot air system. Where hazardous compounds are being dried, this increases the area of exposure and makes cleaning more difficult. Furthermore explosions have occurred in the past in processes where these driers have been used, with subsequent environmental contamination. Fluidized-bed driers should be designed to avoid flammable atmospheres or sources of ignition. The latter might require various measures such as the use of anti-static devices;
- **vacuum driers** may be used in applications where the products are heat sensitive. Release of vapours can be prevented by condensing them directly into the seal water of a vacuum pump, after which they may be recovered. A modern design incorporates tumble drying the material under vacuum. Such a system may be incorporated in a granulator-drier;
- **microwave driers** are gaining acceptance in the pharmaceutical industry, and will be especially useful for drying heat-sensitive products. This technology is ideal for modern dosage forms with low concentrations of active ingredients (<20 mg) in a carefully chosen carrier. A low-volume waste air stream is produced, which can be easily controlled or treated. They have presented no quality problems during single batch drying of a variety of products.

#### **B4.7 Secondary Manufacturing operations**

The aim of secondary pharmaceutical manufacture is to convert the bulk compounds prepared during primary manufacture into a final usable form; for example a tablet, ointment, capsule or cream. It also ensures that the final product is supplied in a safe, well protected manner.

Secondary pharmaceutical manufacture will typically involve several of the following steps:

- receipt of raw materials;
- storage of raw materials;
- sieving/milling/micronizing;

- weighing;
- mixing/blending;
- granulation;
- drying;
- tablet pressing;
- tablet printing;
- tablet coating;
- filling and packing;
- preparation of aerosols.

A brief description of each of these process steps and the environmental impacts associated with them is provided below. A number of these process steps are similar to those displayed by other sectors of the chemical industry and where relevant the reader is referred to Section 2.2 for a general discussion of the basic unit processes and their associated environmental impacts.

#### **B4.7.1 Receipt of raw materials**

See Section on primary manufacture.

#### **B4.7.2 Storage**

See Section on primary manufacture.

#### **B4.7.3 Sieving/milling/micronizing**

Raw materials may be sieved to ensure that there is no foreign material, and then milled as required. These operations may be carried out before or after weighing. If carried out after weighing, adjustment for weight loss may be necessary.

The main environmental impact associated with these process steps is the release of particulates. It should also be noted that these activities may be carried out during primary manufacture.

#### **B4.7.4 Weighing**

Weighing is a crucial element in the manufacture of secondary pharmaceuticals. Careful control of raw materials and solvents is required to ensure that batches meet exacting standards. The main environmental issues associated with weighing are:

- the weighing area should usually be dedicated to one product at a time in order to reduce the chance of cross-contamination;

- the dispensary should be thoroughly cleaned between batches of different products by methods which minimise the use of water.

#### **B4.7.5 Mixing/blending**

The mixing process is vital to all pharmaceutical production. Failure to obtain a correct mix can result in a number of serious effects, such as over dosage of a potent medicine, or inadequate dosage for the required therapeutic effect. Blending may be dry or wet. Wet blending operations use water where possible; otherwise syrups or solvents are used.

The techniques used for mixing follow usual chemical engineering practice, using propeller agitators for mobile liquids and turbine or paddle mixers for more viscous liquids or suspensions. Semi-solids are typically blended with Z-blade mixers, and powders are blended in ribbon blenders, tumbling mixers or high-speed mixers.

When the desired end product is a tablet, a filler, such as starch or sugar, and a binder, such as corn syrup or starch, may be added to the blend. The filler ensures that the active ingredient is diluted to the necessary dose, whilst the binder provides strength and stability for the tablet. Occasionally a lubricant such as magnesium stearate or polyethylene glycol may be added to facilitate equipment operation or to slow disintegration or dissolution of the active ingredient. Once the desired blend has been produced the following steps may be taken to produce the tablet in the final form:

- compression or granulation;
- coating;
- printing.

Each of these steps is discussed in more detail below.

The process is more complex for the production of creams and lotions. The powdered active ingredient is normally mixed with the carrier to produce an homogeneous product with the correct flow properties. The cream may be heated before filling to improve its flow properties.

#### **B4.7.6 Drying**

See Section on primary manufacture.

#### **B4.7.7 Granulation**

Granulation, or agglomeration, is often a precursor to the majority of tablet compression processes and to some encapsulation processes. The aim of granulation is to produce grains of the correct concentration of active ingredient and with the desired physical properties for efficient compression. It should be noted that in granulation the mixture

does not actually go into solution, it forms a dry paste which gradually agglomerates as more and more water is added. The end point is when the agitator senses a certain power consumption. Additionally:

- granulation may not be necessary if the raw materials are suitable for direct compression into tablets;
- powders are often unsuitable for pressing since the varying bulk densities of the individual components often lead to dissociation during storage and in feed hoppers. In addition, they may result in a high degree of dust generation during pressing operations;
- granulation can be wet (composite agglomeration) or dry (press agglomeration). These involve:
  - in wet granulation the active ingredient is powdered and mixed with the filler. This mixture is then wetted and blended with the binder, forming a solution. Coarse granules form which are mixed with lubricants and then compressed into tablets and the tablets dried;
  - dry granulation (slugging) is used when the tablet ingredients are sensitive to moisture, sensitive to the temperatures associated with drying or have sufficient inherent binding or cohesive properties to allow direct compression to form the tablet.
- traditional granulation is carried out in oscillating granulator sieves in combination with tray driers. More modern methods include the use of fluidized-bed granulation driers, high speed mixer-granulators, heated agitator vessels and mixing cones with a shaft rotating around the edge of the cone;
- granulation processes vary from as little as half an hour, and range up to 6 hours to complete.

#### **B4.7.8 Tablet pressing**

Tablets account for the majority of solid medications. They are produced in tablet presses by direct compression of the blended materials or by compression of the granulated, dried mix. A binder holds the powder together and a lubricant is necessary to prevent erosion of the equipment. Important parameters of tableting include speed, quality, reliability and fast changeover of components. Modern tablet presses compress 8000 to 12 000 tablets per minute, and provide automatic control and monitoring of tablet weight. Issues to be considered include:

- tablet presses vary in their degree of containment. Older systems are likely to have open feed and/or collection systems whilst newer systems are likely to be contained. To minimise the release of dust, systems are available that allow the tablets to be sucked upwards from the tablet press and spiral downward into closed collection vessels;
- an automatic system may be included to ensure the rejection of tablets which are either underweight, or overweight;
- newer models of tablet presses may be equipped with metal detectors and tablet de-dusters;
- an alternative to the procedure of granulation, drying and pressing is direct compression. This technique binds the components without the need for granulation and drying. Not only does this technique simplify the processing sequence, but it eliminates the dust, and any volatile organic vapours associated with granulation and drying. The operation is difficult and requires the raw ingredients to be present in a free-flowing, compressible form. Direct compression is established in the USA, but not yet in facilities in the UK.

#### **B4.7.9 Tablet printing**

In some cases information such as the name of the drug and/or the name of the manufacturer may be printed on tablets with a butanol/ethanol based ink. The amount of print added to an individual tablet will be very small but cumulatively over many tens of thousands of tablets is likely to give rise to emissions of VOCs that may require control.

#### **B4.7.10 Tablet coating**

Coating imparts physical strength to the tablet and delays breakup once swallowed. Sugar or film coatings are typically used. Modern tablet-coaters are closed rotating drums, in which the tablets are suspended in a hot-air fluidized-bed. The hot air also serves to dry the atomised coating as it is sprayed onto the tablet. The conditions of air flow, temperature, and the flow and composition of the coating mix, are vital to ensure that the coating dries on the surface of the tablet. The main issues to consider are:

- a certain amount of coating mix always dries in mid-air and forms a very fine dust which must be extracted from the machine;
- where technically and economically feasible, many facilities have converted to water-based coatings. Organic solvents are still used in situations where re-registration is not a viable option, or where slow-release coatings (which are water insoluble) are required. In the latter application, aqueous-based coatings of polymers with a low viscosity may be used;

- direct compression of the granulated coating onto the core tablet is occasionally used as an alternative to wet tablet coating. However, the environmental advantages of solvent-free coating are offset by the need to pre-granulate the coating material;
- after coating the tablet may be sent for a final polishing step. Polishing takes place in a rotary drum and the polishing is imparted by the tablets on each other as they tumble around the drum.

The IChemE (1997) provides a summary of some of the waste minimisation steps taken by a tablet coating pharmaceutical company. Releases of VOCs were reduced by 6.6 tonnes and hazardous waste arisings by 434 tonnes.

#### **B4.7.11 Filling and packing**

Automated mechanical methods of packaging are an integral part of secondary manufacturing, especially for the packaging of sterile products. A single packing line may be used for several products.

The packing line may comprise equipment to perform operations such as tablet counting, weight checks, feeding and separation of tablets, capping, bottle washing, label printing, labelling, packing and palleting.

#### **B4.7.12 Alternatives to tablets**

Tablets are not the only method of delivering the active ingredient to the consumer. Alternatives include:

- **aerosols** are filled, capped, tested and weighed in specialised equipment. The cans and O-rings are fed into an assembly unit through hoppers, and the rings are placed around the neck of the cans. The cans are filled with the product and carrier gas at temperatures as low as -60°C and then capped with the valves in a single operation. The cans are leak tested, weighed and the valve mechanism checked prior to packaging. Traditionally CFC propellants have been used. Butane is widely used in externally-applied products, but is hazardous and flammable. Alternative technologies are emerging which will preclude the need for chemical propellants;
- **capsules** may come in either soft or hard shelled varieties;
  - hard capsules are formed by dipping metal pins into a solution of gelatin. When the pins are withdrawn the gelatin cools and solidifies on the pin. The solid gelatin coating is then trimmed from the pin and filled with the active ingredient;



- soft capsules are formed by placing two continuous gelatin films between rotary die plates. The plates are brought together to form the capsule. As they are brought together the active ingredient is injected between them.
- **liquid dosage** involves the liquid active ingredient being dissolved in the appropriate carrier liquid. Preservatives may be added to prevent the formation of mould and bacterial growth. Sterilization may also be applied to both the product container and the liquid.
- **ointments and creams:**
  - ointments are usually made by blending the active ingredient with a base, such as a petroleum derivative or wax. The mixture is cooled, rolled out and poured into tubes by machines;
  - creams are semi-solid emulsions and are either oil-in-water or water-in-oil, rather than petroleum based. The two phases are usually heated separately, mixed and stirred vigorously to achieve emulsification.

Equipment in which ointments and creams are formed may require cleaning with detergents to deal with the oily residues that are left.

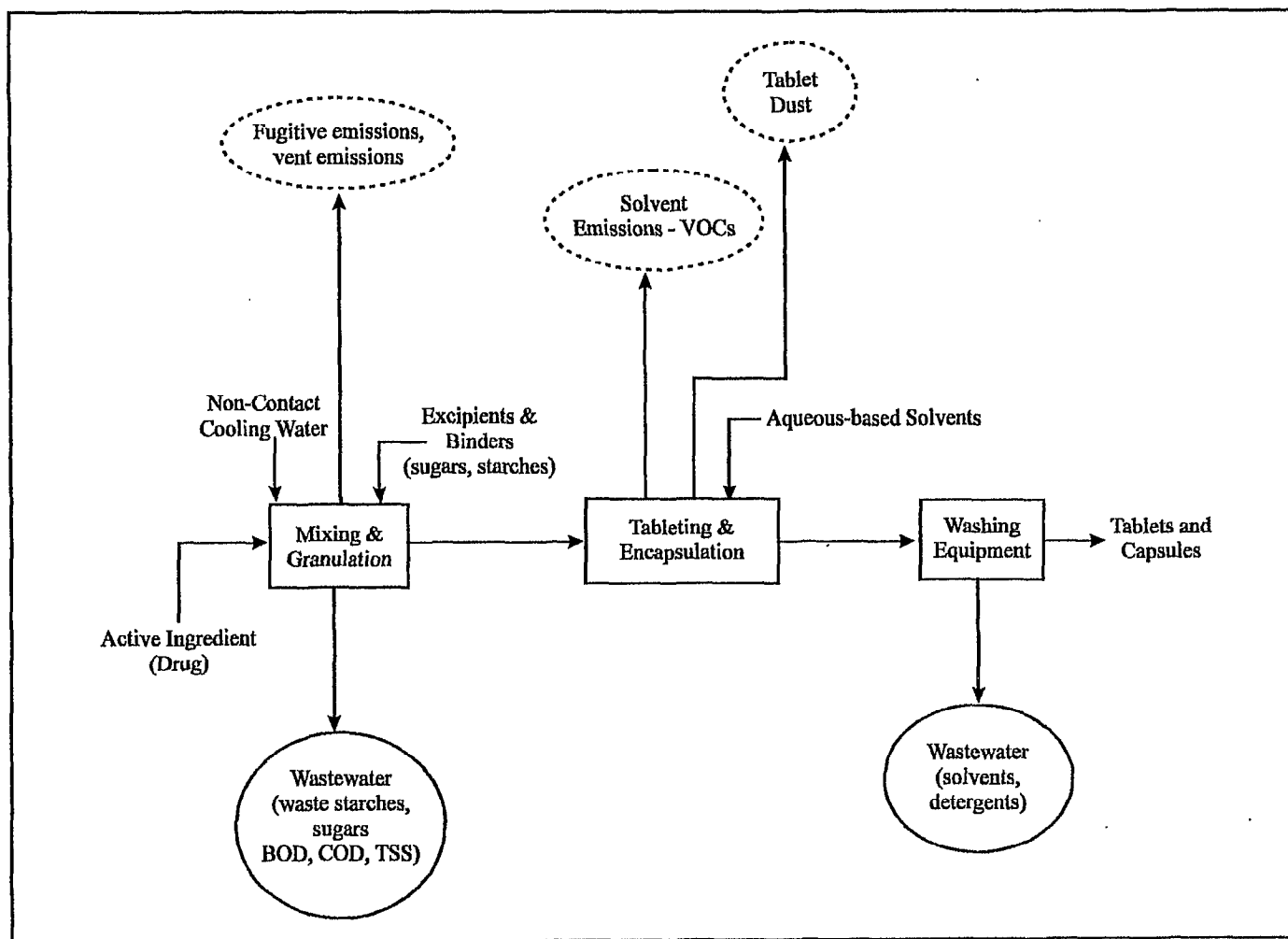
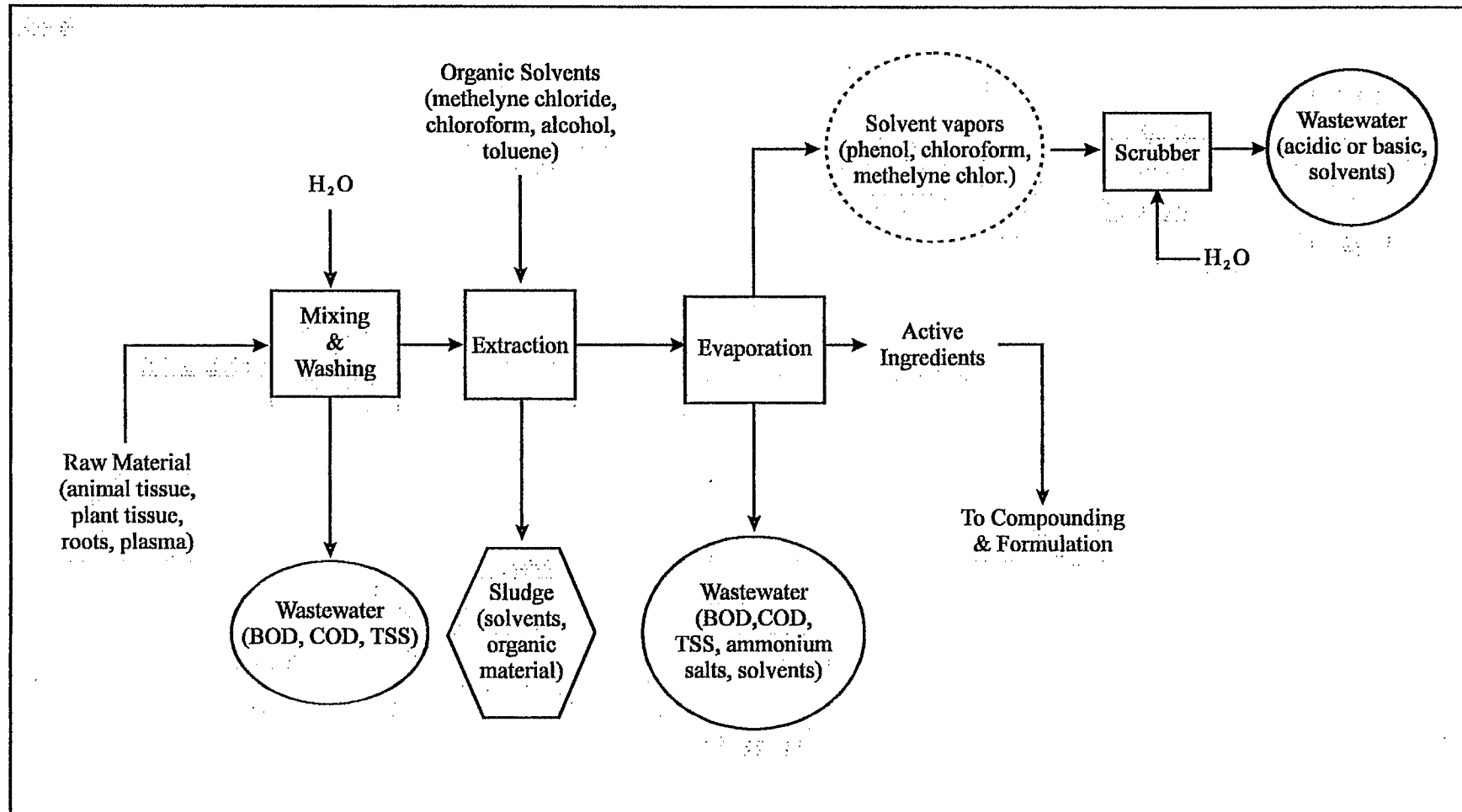


Figure A2.3 Source: Adapted from Economic Impact and Regulatory Flexibility Analysis of Proposed Effluent Guidelines for the Pharmaceutical Manufacturing Industry, 1995



**Figure A2.4 Source: Adapted from Economic Impact and Regulatory Flexibility Analysis of Proposed Effluent Guidelines for the Pharmaceutical Manufacturing Industry, 1995**

## **B5. SULPHONATION AND NITRATION**

### **B5.1 Introduction**

This section contains basic information on the main types of process covered. They may be categorised as:

- aromatic sulphonation and nitration;
- aliphatic sulphation and sulphonation;
- nitrations for explosives manufacture.

A wide range of chemicals are used or generated in organic sulphonation, sulphation and nitration processes. Both solid and liquid products are produced by these processes.

Some processes which fall within the scope of this Guidance Note may not be specifically described. In such cases the most appropriate process technologies and abatement techniques should be inferred by reference to those that are.

Production rates vary considerably between manufacturers, ranging from less than 100 tonnes per annum to in excess of 40 000 tonnes per annum. The processes are usually batch operation frequently employing small-scale multi-product plant. Such plant can usually be modified, as opposed to completely rebuilt, to facilitate the manufacture of new products.

Releases to the environment may be associated with all stages of the manufacturing process from delivery and storage of raw materials, their handling, sampling, transfer and measurement into process reactors; through the process plant and product purification stages to drying, storage, packing and loading. Accidental releases may occur from solids and liquids spillages, gaseous vapour emissions to air from equipment leaks, bursting disc rupture or pressure relief valve opening. A materials loss from these processes occurs during equipment cleaning between different product runs. Unrecycled off-specification intermediates and products generate quantifiable waste streams as do by-products which are not further processed or sold. Liquid and solid (sludge) wastes may be generated as "still" bottoms in product distillation columns for products/by-products separation and solvent recovery operations.

### **B5.2 Product and process types**

Examples of organic sulphonation and nitration processes include the following market sectors: pharmaceuticals, pesticides, dyestuffs and intermediates, and detergents. Some of these processes may be authorised under different sections of the Regulations.

The processes involve a chemical reaction or series of reactions with subsequent separation and purification stages. Any unreacted raw materials may be either recovered and recycled or, treated and ultimately discharged to the environment.

Process stages cover the full range of chemical engineering unit operations and include reaction, liquid/liquid separation, liquid/solid separation, distillation, crystallisation, gas absorption, adsorption, drying, comminution and mixing.

The range of raw materials consumed and the quantities of each material as a batch charge results in the need for extensive storage facilities for raw materials. Storage may employ bulk tanks, silos, drums, sacks and various other packages.

It is common to dispense accurate batch quantities by weighing out part of a raw material package's contents. A range of means is used for dispensing raw materials taken from bulk storage which includes integrating flowmeters and loss in weight measurement systems.

Typical processes currently used in the UK are outlined below. The vast majority of processes are batch operated using conventional stirred tank reactors yielding solid or liquid products. Aromatic sulphonations and nitrations are electrophilic substitution reactions. The reaction conditions selected should be such as to maximise the positional specificity of the substitution, minimise the formation of by-products of non-specific substitution or over-substitution whilst ensuring high yield of desired product. Variations in reagents used and operating conditions proposed by operators should be scrutinised from the point of view of waste minimisation and cleaner production considerations as part of the overall philosophy of integrated pollution control.

### **B5.3 Aromatic sulphonation/nitration**

Sulphonation is often accomplished with concentrated sulphuric acid, but it can also be affected with fuming sulphuric acid (oleum), sulphur trioxide, chlorosulphonic acid or, less commonly, other reagents. Reagents having a wide variety of activity are available to suit both highly active and inactive starting molecules.

Most aromatic compounds can be nitrated by the use of a wide variety of nitrating agents. The most common reagent is a mixture of concentrated nitric and sulphuric acid ("mixed acid"). For active substrates the reaction can be carried out with nitric acid alone in water, acetic acid or acetic anhydride. These milder conditions being favoured for labile compounds such as aminophenols.

Newer, milder nitration methods for acid-labile substrates include the use of small amounts of electrolytically generated dinitrogen pentoxide to provide an efficient source of nitronium ion, without accompanying high acidity. Only small scale generation facilities are available at present.

### **B5.3.1 Solid product**

The manufacture of solid products involves organic feed material being charged to a stirred tank reactor together with a sulphonating or nitrating agent. The reactions are exothermic and are generally carried out at atmospheric pressure. Reaction temperatures vary according to the product being made but generally lie in a range between zero and 130 °C, usually around 100 °C.

For example, in the sulphonation of nitrobenzene to manufacture nitrobenzene sulphonic acid, nitrobenzene is charged from bulk liquid storage via a weigh vessel into the reactor. (The weigh vessel is vented to the general scrubber system). Sixty five percent oleum is added by a weigh vessel which is vented to the sulphur trioxide scrubber. The reactor is charged over a period of 6 hours, followed by a 10 hour reaction time. Reaction temperature is controlled by the use of steam, cooling water or chilled water in the reactor jacket. The reactor is vented to the sulphur trioxide/sulphuric acid mist scrubber.

On completion of reaction the reactor contents may be discharged into a quench or drown-out vessel. The drown-out vessel is vented to the sulphur trioxide/sulphuric acid mist scrubber.

The solid product is filtered in a pressure filter, with much of the mother liquor recycled to the reactor, the remainder is sent to waste. The waste typically contains 20 to 30% sulphuric acid with small amounts of organic contaminants and is neutralised with lime to produce gypsum (calcium sulphate) which is sent for landfill to a licensed waste management facility.

The reaction product is washed with water on the filter giving a low acidity waste (less than 2% sulphuric acid) which is neutralised by passage through limestone beds before passing to the effluent treatment system.

The sulphur trioxide scrubber is ceramic packed and uses 98% sulphuric acid to absorb sulphur trioxide and water vapour evolved during the reaction. The gases then pass through a candle filter to eliminate mist.

For nitration reactions the gases are also scrubbed with a NO<sub>x</sub> scrubber using a weak caustic soda solution. Gases fed to the scrubber, which is usually of plastic construction, are diluted with air to convert some NO to NO<sub>2</sub> which is the only form of NO<sub>x</sub> absorbed by these scrubbers.

### **B5.3.2 Liquid product**

As with solid product, the organic feed is charged to a reactor with the sulphonating or nitrating agent. Thus for example in the nitration of benzene using mixed acid, nitrobenzene is produced in a series of continuously stirred tank reactors.

The sulphuric acid is continuously recycled through the first reactor of the series to which benzene, nitric acid and concentrated sulphuric acid are added. The reaction temperature is controlled at 65 to 68 °C using a closed circuit cooling system.

After reaction the reaction mixture is cooled to 35-40 °C and nitrobenzene and sulphuric acid separated by gravity. The nitrobenzene is washed with water and then with 1.5% caustic soda solution to remove sulphuric acid and is then steam stripped to remove excess benzene, which is recycled to the first nitrator. The stripper bottoms constitute nitrobenzene and water which are separated by gravity. Water is partially recycled to the nitrobenzene washing stage and the excess goes to caustic effluent treatment.

Seventy percent sulphuric acid remaining after nitration and gravity separation from nitrobenzene is washed with benzene to extract remaining nitrobenzene. The benzene is returned to the first nitrator. Sulphuric acid is reconcentrated in a separate plant to 91% for reuse in the nitration process.

The use of continuously stirred tank reactors with waste stream recycling has considerable energy and environmental advantages over single batch operations. The need to dispose of or reconcentrate the sulphuric acid remaining when the nitration reaction is completed is minimised with both energy and environmental benefits.

As an alternative, it is also possible with equal environmental advantages and rather less energy efficiency advantages to treat the 70% spent sulphuric acid by heating at low pressure in a glass heat exchanger to generate benzene vapour and nitrogen dioxide. Recovery by absorption then enables around 90% of the benzene and nitrogen dioxide dissolved in the sulphuric acid to be recovered for recycle to the nitration reactor. The remaining off-gas is passed to a gas incineration unit. After the heating stage the acid flows into glass evaporation vessels equipped with tantalum heating elements that are resistant to acid up to 180 °C. The water is evaporated from the aqueous acid until the acid has a concentration of over 80%. From the evaporator the reconcentrated acid flows via the heat exchanger and cooler to a storage tank for further concentration, reuse or sale.

### **B5.3.3 A typical aromatic sulphonation and a new sulphonation process**

Naphthalene sulphonic acid, an intermediate in dyestuff and plastics manufacture, has traditionally been produced from naphthalene by reaction with sulphur trioxide and sulphuric acid (as solvent). Sodium chloride and caustic soda are added to separate the product, so recovery of the sulphuric acid is not possible. Yield of the naphthalene sulphonic acid is approximately 45% (as a percentage of the naphthalene used). The acidic effluent passes to a clarifier before being discharged via effluent treatment.

An alternative process has been developed that:

- improves significantly the yield of the naphthalenesulphonic acid;
- enables the spent sulphuric acid to be recovered/recycled.

Naphthalene and sulphur trioxide are dissolved in an organic solvent (a chlorinated hydrocarbon) and reacted at low temperature. The naphthalene sulphonic acid is subsequently mixed with water and sulphuric acid. The organic solvent is separated, recovered and recycled. The sulphuric acid solution of naphthalene sulphonic acid is cooled and the crystallised product recovered. The salt free, spent sulphuric acid is reconcentrated and recycled.

Recovery of the solvent also uses low energy technology in that it is dried by means of a pulsation column rather than the more conventional distillation method.

Effluent COD levels are considerably reduced and in addition there is a significant increase in product yield.

### **Potential Release Routes**

The principal releases from sulphonation processes are:

#### **Releases to air**

- oxides of sulphur and sulphuric acid mist from reaction vessels and sulphuric acid, oleum and chlorosulphonic acid from storage tank vents;
- hydrogen chloride from reactor vents or storage tank vents (when chlorosulphonic acid is used as a sulphonating agent);
- volatile organic compounds such as benzene released from reactor vents and storage tank vents.

#### **Releases to water**

- spent sulphuric acid from the process;
- dilute sulphuric acid from product washing;
- dilute caustic soda from product washing;
- sulphuric acid from sulphur trioxide scrubbers;
- trace organic compounds from cross contamination of aqueous wash streams.



### Releases to land

- trace organic compounds in contaminated calcium sulphate sent to landfill after lime neutralisation of sulphuric acid waste streams.

The principal releases from nitration processes are:

### Releases to air

- oxides of nitrogen from nitric acid storage tanks, reactor vessel vents and NO<sub>x</sub> scrubbers;
- oxides of sulphur from sulphuric acid or oleum storage tanks, reactor vessel vents and SO<sub>3</sub> scrubbers;
- trace organic compounds such as benzene from storage tank vents and reactor vessel vents.

### Releases to water

- spent sulphuric acid from the process;
- dilute nitric and sulphuric acid from product washing;
- dilute caustic soda from product washing;
- spent caustic soda containing sodium nitrite and sodium nitrate from NO<sub>x</sub> scrubbers;
- organic compounds from cross-contamination of aqueous wash streams.

### Releases to land

- none.

## B5.4 Aliphatic sulphation/sulphonation

Sulphur trioxide is used to sulphate long chain fatty aliphatic alcohols and ethers and to sulphonate alkylates in a variety of continuous process reactor types. The sulphur trioxide is used in the vapour phase, generally diluted with air. The sulphur trioxide is derived either from liquid SO<sub>3</sub> or generated from molten sulphur via oxidation to give an SO<sub>2</sub>/SO<sub>3</sub> mixture which is catalytically converted to SO<sub>3</sub> at high temperatures.

Two different types of sulphator/sulphonator are in common usage:

#### **B5.4.1 The Baker Perkins Reactor**

The Baker Perkins reactor uses a series of alternate static and rotating plates to give intimate mixing of reaction components. Using this type of reactor, sulphur trioxide from a steam-heated falling film or similar evaporator, or from an SO<sub>2</sub> oxidation unit is diluted with dry air to give a 4% sulphur trioxide stream. This is introduced along the length of the reactor containing the organic substrate and the temperature is kept below 60°C by a cooling jacket.

The product is discharged to a centrifuge where liquid is separated from air and surplus sulphur trioxide. The gas stream is passed to a cyclone for separation of residual liquid which joins the main liquid flow and the acidic product containing unstable acid sulphate is neutralised with caustic soda, ammonia or other base to give a stable product solution. The cyclone gas is ducted to an electrostatic precipitator (ESP) to remove organics and any sulphuric acid resulting from excess sulphur trioxide and water produced in the reaction. The resulting gas stream is vented to atmosphere via a stack. The material collected from the electrostatic precipitator is a viscous black acidic sludge which is taken away for disposal at a licensed waste management facility. The moving parts of the plant require maintenance and seals are a potential source of leakage.

#### **B5.4.2 The Falling Film Tubular Reactor**

In the falling film tubular reactor, air is compressed and dried and mixed with sulphur trioxide to give a 2½% sulphur trioxide concentration. The gas mixture is passed through a de-mister to remove any oleum droplets which would otherwise destroy the falling film in the sulphonator and affect the product quality.

The alkylate or ethoxylate starting material is pumped into the top of the reactor and flows down the inside of the tube as a thin film. Sulphur trioxide reacts in the film, the heat of reaction being removed by cooling water in the shell of the reactor. The product separates from the air and surplus sulphur trioxide in the bottom of the reactor. The gases pass through a cyclone to remove entrained product and are then ducted to an electrostatic precipitator (ESP) followed by a candle filter and then a caustic scrubber. To suppress a visible plume formation, the tail gases are heated using waste heat from the sulphur combustion system before release to atmosphere via a stack. The sludge and spent liquor resulting from the ESP and scrubber is disposed of to a licensed waste management facility. The liquid product is pumped into neutralisation loops (2 in series) where a base (usually caustic soda and water) is added in metered amounts. Heat of neutralisation is removed in a heat exchanger.

Although acid sulphate products require treatment with a base to stabilise them, sulphonic acid products do not. They do, however, require a soaking period for the reaction to proceed to completion.

### **B5.4.3 Potential Release Routes**

#### **Releases to air**

- oxides of sulphur from the electrostatic precipitator vent;
- mists containing organic compounds from the electrostatic precipitator;
- fugitive releases of oxides of sulphur from the SO<sub>3</sub> production facility.

#### **Releases to water**

- sulphuric acid from the de-mister;
- organic sulphonic compounds from surface drains;
- surplus sulphuric acid from the acid scrubber;
- fugitive releases of sulphuric acid from the SO<sub>3</sub> production facility.

#### **Releases to land**

- sulphonated organics from electrostatic precipitator sludge to landfill.

### **B5.5 Nitration for explosives manufacture**

The extreme sensitivity of the product requires the feedstock, for example glycerine, to be nitrated with mixed acid at about 0 °C. Techniques are employed which ensure a minimum product inventory within the reaction system.

The resulting emulsion of nitroglycerine and spent acid is chilled and separated. Part of the spent acid is recycled whilst the remainder is sent for denitration where the nitric and sulphuric components are separated by distillation.

The nitroglycerine product contains a small percentage of nitric acid and is washed first with water and then sodium carbonate solution from which the final product is separated as a heavy organic layer. Aqueous washings are sent to effluent treatment.

### **B5.5.1 Potential Release Routes**

#### **Releases to air**

- oxides of nitrogen from storage tank or reactor vents;
- oxides of sulphur from storage tank or reactor vents;
- oxides of nitrogen from gas scrubbing.

#### **Releases to water**

- spent caustic soda from the nitration vent scrubber;
- spent nitric acid from the denitration process;
- spent sulphuric acid from the denitration process;
- dilute nitric acid from tail gas scrubbers;
- dilute nitric acid from the product washing stream;
- small quantities of organic feedstock or product in the above aqueous streams.

#### **Releases to land**

- none.

## **B6. HALOGENATION**

### **B6.1 Introduction**

Processes involving the halogenation of organic chemicals are employed in the manufacture of a wide range of commodities including pharmaceuticals, pesticides, dyestuffs and intermediates, photographic chemicals, flame retardants, plastics/rubber chemicals and cosmetics.

Halogenation reactions involve the introduction of one or more halogen atoms into an organic chemical. This may occur by:

- addition;
- substitution;
- exchange.

Such reactions may be carried out with the halogen, the hydrogen halide or a halogenating agent such as a metal halide, sulphuryl chloride or thionyl chloride. The organic chemical to be halogenated may be or derived from a wide range of substances including for example acids, saturated and unsaturated hydrocarbons, alcohols, phenols and amines.

Many halogenation processes are carried out on a small scale using multi-purpose batch plant. Such plants can usually be adapted to facilitate the manufacture of alternative products. Typically manufacturing capacity for such processes is small and normally well below 500 tonnes per annum.

There are, however, some continuous processes carried out on dedicated plants with an installed capacity of many thousands of tonnes per annum. These include, for example, plants for the production of aliphatic chloro compounds such as ethylene dichloride, perchloroethylene, trichloroethylene, or plants for the manufacture of ethylene dibromide, brominated flame retardants, fluorocarbons, chlorofluorocarbons and hydrochlorofluorocarbons.

Some halogenated organic compounds are highly persistent when released into the environment. The Montreal Protocol concerns substances which deplete the ozone layer. EC Directive 90/415/EEC covers releases to water from the manufacture and use of 1,2 dichloroethane, trichloroethylene, perchloroethylene and trichlorobenzene.

Owing to the very extensive range of processes that may be included within the scope of this section it is not considered possible to describe the chemistry in any detail. The consequence of many halogenation reactions is that excess halogen together with hydrogen halide will be released from the reaction and this release will need to be treated, prior to release to the environment, by suitable abatement plant.

The product of reaction is subsequently treated to separate it from unwanted by-products, solvents, unreacted raw materials, entrained gases, catalyst etc. The halogenated product may also be used as a precursor for further reactions without prior isolation.

Unreacted raw materials should be recovered and recycled. Solvents should be recovered and recycled, preferably directly back to the originating process or by on-site or off-site recovery within the chemicals industry. Incineration with flue gas scrubbing should be used for disposal of unrecoverable solvents and wastes, such as still bottoms, from recovery operations.

## **B6.2 General process descriptions**

### **B6.2.1 Batch processes**

Batch halogenation processes typically involve charging a reactor with the chemical to be halogenated. This may be as a pure chemical, a solution or a suspension. In some multi stage syntheses it may have been generated in situ as the product of the previous chemical reaction step.

Liquid chlorine is usually vaporised then sparged through the mixture. Bromine is used in either the liquid or vapour form. Iodination reactions can be accomplished using iodine monochloride. Fluorinations, may be carried out using a halogen exchange technique or using hydrogen fluoride.

Other agents used to carry out halogenations include thionyl chloride, sulphuryl chloride and phosphorus chlorides. Some halogenation reactions are carried out in the presence of catalysts or under ultra violet irradiation.

The choice of agent used for carrying out a halogenation reaction will depend on the precise process chemistry involved. Where it is possible to choose between several halogenating agents the selection should be made on the basis of preventing or minimising releases taking into account raw materials, handling problems, minimisation of waste by-product streams, and maximising conversion efficiency.

The very wide range of reactants and the quantities of each substance required for each charge results in the use of a wide variety of raw materials storage facilities. Quantities of reactants required are normally dispensed by weight. Dispensing from bulk storage is usually accomplished by the use of integrating flowmeters and/or load cells.

Processing is commonly carried out with the batch identity retained for product analysis and yield data. Material balances may be used in conjunction with product analysis to identify by-product and waste streams.

### **B6.2.2 Continuous processes**

In large scale plants an organic feedstock is reacted with a 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 or halide should be recovered and returned to the process or other productive use wherever practicable.

Examples of these processes include the reaction of ethylene and chlorine to form ethylene dichloride and its subsequent conversion to vinyl chloride which is described in IPC GN S2 4.01. Ethylene dichloride 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 (HCFCs) 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.

The main halogenating agents are summarised in the Table below.

Halogenating agent	Advantage	Disadvantage
Chlorine	<ul style="list-style-type: none"> <li>• Many reactions will generate only gaseous by-product streams, which are easily removed from the off gas;</li> <li>• On completion of the reaction only small amounts of chlorine usually remain.</li> </ul>	<ul style="list-style-type: none"> <li>• Sophisticated storage and handling facilities are normally required.</li> </ul>
Bromine	<ul style="list-style-type: none"> <li>• As for chlorine;</li> <li>• Can be contained in small, easily handled containers.</li> </ul>	<ul style="list-style-type: none"> <li>• As for chlorine.</li> </ul>
Iodine	<ul style="list-style-type: none"> <li>• Readily available;</li> <li>• Does not require sophisticated storage facilities.</li> </ul>	<ul style="list-style-type: none"> <li>• Charging of solids to the reaction vessel may require special solids handling equipment;</li> <li>• Difficulties with certain waste disposal routes.</li> </ul>
Thionyl chloride/ Sulphuryl chloride	<ul style="list-style-type: none"> <li>• Many reactions will generate gaseous by-product streams which are most easily removed from the off gas;</li> <li>• Readily available in containers up to 200 litres;</li> <li>• Does not require sophisticated storage facilities.</li> </ul>	<ul style="list-style-type: none"> <li>• Reacts violently with water, alcohols etc.;</li> <li>• On completion of the reaction considerable excess quantities can remain and these have to be removed by distillation;</li> <li>• Removing the reaction product may be difficult.</li> </ul>
Phosphorus tri and penta chloride	<ul style="list-style-type: none"> <li>• Readily available in containers up to 150 litres and in bulk;</li> <li>• On completion of the reaction may be removed by filtration.</li> </ul>	<ul style="list-style-type: none"> <li>• Charging of the solids to the reaction vessel may require special solids handling equipment;</li> <li>• Effluent containing phosphorus compounds may require specialist treatment;</li> <li>• Reacts violently with water and fumes on contact with moist air.</li> </ul>

Halogenating agent	Advantage	Disadvantage
Aluminium chloride	<ul style="list-style-type: none"> <li>• Readily available;</li> <li>• Does not require sophisticated storage facilities;</li> <li>• Can be used to carry out chemical reactions to produce substances which would be difficult to make using other approaches.</li> </ul>	<ul style="list-style-type: none"> <li>• Fumes readily in contact with moist air generating hydrogen chloride and aluminium hydroxide;</li> <li>• Generates a considerable volume of aqueous effluent containing aluminium salts. This effluent is usually highly acidic;</li> <li>• Charging of solids to the reaction vessel may require special solids handling.</li> </ul>
Hydrogen halides	<ul style="list-style-type: none"> <li>• Readily available in anhydrous form or aqueous solution;</li> <li>• May generate no gaseous by-product.</li> </ul>	<ul style="list-style-type: none"> <li>• Sophisticated storage and handling facilities are often required.</li> </ul>

### B6.2.3 Potential releases associated with halogenation processes

Dependent on the particular process, the following releases may arise.

#### Releases to air

Free halogens, hydrogen halides, sulphur dioxide, process purge gas and trace organics in the gases exiting scrubber(s). Fugitive releases from process vents may also contain these gases.

#### Releases to water

These can arise from a number of sources including spent liquors from gas scrubbing, sealing water from liquid ring vacuum pumps, overflows from barometric legs on ejector systems etc., and may contain:

- salts from halogen and/or halide absorption;
- sodium hydroxide;
- free halogens;
- hydrogen halides;
- aluminium salts;
- traces of organic materials including halogenated solvents.

#### Releases to land

- tars from distillations;
- unreacted raw materials;
- spent catalyst.



## **APPENDIX C ECONOMICS**

### **C1. INTRODUCTION**

This Appendix considers the economic implications of utilising BATNEEC in the sector covered by this study. Two approaches to integrate economics with techniques have been considered, these are:

1. Sector affordability (Section C2) - i.e. the economics of the sector are such that further investment in pollution prevention and control would make it too vulnerable to competition and is likely to drive UK companies out of business;
2. Not Entailing Excessive Cost (Section C3) - this is applied on a process specific basis and considers the balance between the marginal environmental improvements that can be achieved for a given level of investment in techniques. The Agency has already issued Generic guidance on the identification of BATNEEC (HMSO 1997e), this study provides more specific guidance on the application of BATNEEC to the sector of interest;

The approaches are complementary - the analysis of sector affordability provides a very general picture of the issues, while NEEC considers issues on a site by site basis. Both of these approaches are considered in more detail below.

### **C2. SECTOR AFFORDABILITY**

#### **C2.1 Introduction**

The purpose of this assessment of sector affordability is to draw upon a full range of information to gain an independent overview of the sector under investigation and the economic factors likely to affect it. The first step is to define the sector of interest. This is done in Section C2.2. The methodology for assessing sector affordability is discussed in Section C2.3 together with the underlying economic principles that have been utilised. A number of sector affordability indicators relating to market, operating and financial conditions, are discussed in Section C2.4. Section C2.5 presents an overview of the assessment of sector affordability. Section C2.6 presents the results for the affordability indicators. Section C2.7 gives the results of a number of simulated cost escalation scenarios in terms of their affordability implications for the sectors of interest. Section C2.8 discusses the conclusions.

#### **C2.2 Sector definition**

Before undertaking the assessment of sector affordability it is first necessary to clarify the definition of the sector of interest. This is because the sector definitions used by the IPC system are not the same as those used to report financial and economic data.

In defining the sector of interest (the IPC sector) the link between the companies operating the processes and the markets in which they operate has been made through the use of the IPC authorisation database. The IPC database has been linked to existing commercial databases containing financial and economic information about the companies. Measurement errors are introduced through the accounting conventions used in reporting financial data. As a result the financial and economic information may not relate to the process user itself but to a financial accounting unit within which it operates (e.g. the division of a larger company, an in-house department within a larger organisation or even a financial holding company which has title over the assets). In addition, the assessment of sector affordability undertaken here relates only to a subset of companies (approximately 50%) for which financial data were obtainable.

Total employment of the companies for which information could be obtained was 47 000. Grossing up using the average employment of these companies suggests a total employment in all firms with an authorisation of over 90 000.

The IPC database has been used to define the markets into which firms with the process authorisation operate. The following table (Table C1) summarises the number of firms within 1992 Standard Industrial Classifications (SIC).

**Table C1 Industrial Classifications (SIC92) of Companies covered by this study**

SIC 92 Group	Number	%	SIC 92 Code
Manufacture of basic pharmaceutical products	23	8	15
Manufacture of food products	6	2	24
Manufacture of other chemical products nec (in man made fibres)	23	8	24
Manufacture of other organic basic chemicals	69	25	24
Manufacture of paints, varnishes and similar coatings, printing ink and mastics	9	3	24
Manufacture of pesticides and other agro-chemical products	4	1	21
Manufacture of pulp and paper products	4	1	24
Manufacture of soap and detergents, cleaning and polishing preparations	6	2	24
Manufacture of Textiles	8	3	17
Other	19	7	20,45,50-52, 60,65,74,90
Other manufacturing	29	10	23,26-36
Research and development	6	2	73
Manufacture of other plastic and rubber products	31	11	25
Wholesale of chemical and other products	40	14	51
Grand Total	277	100	

The majority of companies (58%) are engaged in either the manufacture of, or wholesale, of chemicals as their primary business activity. Rubber and plastic product manufacture is also important (11%). Apart from these major groupings however, the companies with authorisations are spread amongst a very diverse set of industries including the manufacture of food and beverages, textiles, fuel, construction, transport, and sanitary services. The characteristics of these SIC sectors are discussed in more detail below:

### **C2.2.1 Manufacture of basic pharmaceutical products**

This sector includes companies involved in the research, development and production of medicinal active substances to be used for their pharmacological properties in the manufacture of medicaments. Companies involved in the processing of blood, and glands and the manufacture of chemically pure sugars are also included.

### **C2.2.2 Manufacture of Food Products**

This sector includes companies producing refined oils and fats as well as further processing. Other companies represented are involved in the manufacture of yeast, powdered or reconstituted eggs.

### **C2.2.3 Manufacture of other chemical products not elsewhere classified**

This sector includes companies involved in the manufacture of a variety of chemical products including:

- peptones, peptone derivatives and other protein substances;
- chemically modified oils and fats;
- materials used in the finishing of textiles and leather;
- powders and pastes used in soldering, brazing or welding;
- substances used to pickle metals;
- prepared additives for cements;
- activated carbon, lubricating oil additives, prepared rubber accelerators, catalysts and other chemical products for industrial use;
- anti knock preparations, anti freeze preparations, liquids for hydraulic transmission;
- composite diagnostic or laboratory and drawing ink;
- manufacture of writing or drawing ink.

In addition the manufacture of glues and gelatines and the manufacture of man made fibres is also included in this group.

### **C2.2.4 Manufacture of other organic basic chemicals**

This sector has the largest representation in the sample and involves a wide variety of manufacturing operations, including:

- manufacture of cyclic and acyclic hydrocarbons and alcohols;
- mono and polycarboxylic acids;
- oxygen function compounds;
- nitrogen function compounds;
- wood distillation products;
- manufacture of charcoal;
- production of pitch and pitch coke;
- manufacture of synthetic aromatic products;
- distillation of coal tar.
- Manufacture of paints etc.

#### **C2.2.5 Manufacture of paints etc.**

This is a small sector with nine companies represented. These companies will be involved in the manufacture of paints, varnishes, enamels and lacquers, prepared pigments, opacifiers and colours, vitrifiable enamels and glazes and engobes and similar preparations. Also included are companies who manufacture organic composite solvents and thinners and prepared paint or varnish removers.

#### **C2.2.6 Manufacture of pesticides and other agro-chemical products**

This sector, of which four companies in the sample are represented, involves companies engaged in the manufacture of insecticides, rodenticides, fungicides, herbicides, anti-sprouting products, plant growth regulators, disinfectants and other agro-chemical products.

#### **C2.2.7 Manufacture of pulp and paper products**

The sector includes companies involved in the manufacture of paper and paperboard intended for further processing; the coating, covering, and impregnation of paper and paperboard; the manufacture of creped or crinkled paper; and the manufacture of cellulose wadding and webs of cellulose fibres. In addition the sector includes the manufacture of cartons, boxes, cases and other containers and the manufacture of paper stationary (including, self copy paper and gummed and adhesive paper).

#### **C2.2.8 Manufacture of soap and detergents, cleaning and polishing preparations perfumes and toilet preparations.**

This sector includes companies who may be involved in the manufacture of organic surface active agents, soap, crude glycerol and surface active preparations such as washing powders, textile softeners, and dish-washing preparations. Companies involved in the manufacture of cleaning and polishing preparations are also included. Companies may be involved in the manufacture of cleaning and polishing products such as preparations for perfuming or deodorising rooms, artificial and prepared waxes, polishes and creams for leather, wood, coach-work , glass and metal, and

scouring pastes and powders. Companies involved in the manufacture of perfumes and toilet preparations are also included.

### **C2.2.9 Manufacture of Textiles**

This sector includes the preparation and spinning of cotton type fibres, the finishing of textiles (e.g. bleaching, dyeing) and the manufacture of knitted and crocheted articles. The manufacture of other textiles is also included such as the metalised yarn, impregnated coated, covered or laminated fabrics.

### **C2.2.10 Other**

This sector involves a wide range of non manufacturing companies such as the installation of electrical wiring and fittings, the sale of motor vehicles, specialised retail (wallpaper, weapons and ammunition, flowers plants seeds and fertilisers), those involved in freight transport, monetary inter-mediation (banks etc.), management of holding companies, and sanitary services.

### **C2.2.11 Other manufacturing**

This sector includes a very large variety of activities such as:

- manufacture of refined petroleum products;
- shaping and processing of flat glass;
- production of abrasive products;
- basic iron and steel production;
- aluminium production;
- treatment and coating of metals;
- manufacture of bearing, gears, gearing and driving elements;
- manufacture of agricultural and forestry machinery;
- manufacture of electricity distribution and control apparatus;
- manufacture of television and radio receivers etc.;
- manufacture of medical and surgical equipment;
- manufacture of industrial process control equipment;
- manufacture of spectacles and un-mounted lenses.

### **C2.2.12 Research and Development**

This includes companies involved in research and experimental development in science and engineering.

### **C2.2.13 Manufacture of plastic and rubber products**

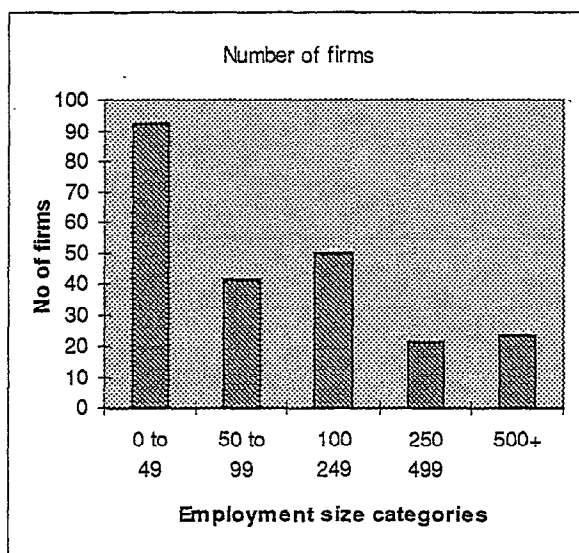
Companies in this sector may be involved in a number of rubber and plastic products manufacture including the manufacture of semi-finished and finished rubber products

(tubes, pipes, belts, hygienic and contraceptive devices, rubberised textiles thread and rope), plastic tableware, headgear, insulating and other fittings.

#### C2.2.14 Wholesale of chemical and other activities

This sector is a relatively large group within the sample covering 40 companies. It includes the wholesale of chemical products (industrial chemicals, fertilisers and agro chemical products, plastics and rubber). Also represented are companies involved in the wholesale of construction machinery, the wholesale of textiles, metals and metal ores.

It is clear from this examination of the SIC classifications that while the companies can, to an extent be classified as operating within the "chemical industry" there are a large number of companies who, although having authorisations for speciality chemicals manufacture, operate in very different markets. This presents considerable problems in terms of the assessment of sector affordability, since in effect the companies in this sector appear to be a microcosm of the economy at large. An assessment of the affordability of all sectors is beyond the scope of this analysis. The primary focus, therefore, is on the chemicals sector, and in particular the stand alone and divisional operators. It is assumed that an analysis of the affordability of this sector provides results which can be translated to other sectors. The results of analysis of the employment size of companies is presented in the Figure C1.



**Figure C1** Frequency of companies in employment bands

Companies with less than 250 employees are generally regarded as being small and medium sized enterprises (SMEs). This figure demonstrates the importance of SMEs in this sector.

## C2.3 Methodology and Economic Principles

The question of affordability relates to whether further investment in pollution prevention and control would make the IPC sector too vulnerable to competition and thus drive UK companies within it out of business. This section outlines the methodology that has been adopted to assess sector affordability.

The issue of affordability must be seen in terms of the sector's position with and without intervention by the Agency. The various markets within which the companies operate may have very different financial characteristics and economic prospects. Some sectors operate in markets characterised by very low profit margins and a susceptibility to cost/price increases. Others may have high profit margins which may reflect high levels of efficiency, unique skills or the ownership of patents.

Affordability in the context of the IPC sector does not imply affordability by each individual company covered by it. The assessment of affordability at an aggregate scale must focus on the principle cause and effect relationships within the IPC sector. Adoption of BAT by existing IPC process operators may lead to a cost increase. This is not necessarily the case but it is the focus of this assessment as it defines the limiting situation. The impact of cost increases may be diverse depending on other operating and market conditions. A variety of impacts can be identified - these impacts can be thought of as strategies for dealing with cost escalation. The next step is to identify unwanted outcomes and define indicators of susceptibility to these outcomes. These strategies, outcomes and indicators form the framework for the assessment of sector affordability and are summarised in Table C2 below.

**Table C2 Strategies, outcomes and indicators for cost increases**

Strategy	Outcome (threats)	Indicators (susceptibility)
<b>Pass through Cost</b> increase passed through to consumers via increased prices	Either demand is sustained at the higher price or demand is reduced, leading to a fall in sales and consequent reductions in scale of operations.	<b>Market</b> <ul style="list-style-type: none"> <li>• price strategies,</li> <li>• degree of market protection (patents, barriers to entry etc.),</li> <li>• foreign competition at home and in overseas markets (not subject to cost increase)</li> </ul>
<b>Pass back</b> Cost increase leads to efficiency drive on input prices, resource waste etc.	Required efficiency savings are found or there is no further scope.	<b>Operational</b> <ul style="list-style-type: none"> <li>• scope for efficiency improvements (existing slack, etc.)</li> </ul>
<b>Absorption</b> Cost increase leads to reduction in profit margins	May reduce returns to shareholders, reduced ability to raise finance (debt and equity) for future expansion.	<b>Financial</b> <ul style="list-style-type: none"> <li>• financial ratios, (profitability, return on capital, assets and liabilities)</li> <li>• cost of investment funds.</li> </ul>

BATNEEC intervention may lead to unit cost increases for the process and hence eventual product. Cost increases can be dealt with through a variety of strategies, each of which will have an associated outcome determined by market, operating conditions and financial conditions. The ability to fully pass through costs without a detrimental impact upon the sector means there is no affordability issue, since final consumers will ultimately be paying for the environmental improvements which are achieved (and from which they ultimately benefit).

The inability to fully pass through costs or unwanted outcomes from cost pass through are likely to be determined by existing and future market conditions, these include:

- competition from foreign firms not subjected to the BATNEEC cost increase mean that pass through possibilities are curtailed. A pass through strategy would lead to declining market share for UK based firms;
- the inability to compete on non-price elements of the product. Insufficient differentiation of the product will limit the ability of the UK firms to pass through cost increases and retain market share (e.g. through the use of customer loyalty);
- differences in the cost pattern of firms mean that large or leading firms may be able to absorb costs increases better than smaller firms. Smaller firms may therefore need to pass through costs and lose market share to larger firms leading to a concentration of activity in the industry.

The alternative to full or partial cost pass through is to pursue operating cost reductions (pass back). The efficacy of such cost push efficiency will depend upon the scope for efficiency savings in other aspects of the businesses' operations. Efficiency savings are likely to be more prevalent where a degree of slack has built up in the producers (over-manning, high wage costs etc.). Seeking efficiency savings as a result of cost increases can be thought of as cost pass back, in that the industry attempts to pass back the consequences of the cost increases up the production line to individual factors of production.

The inability to avoid detrimental outcomes through pass through and pass back strategies means that there will need to be absorption. Absorption is in many ways related to efficiency but is separated in this assessment because efficiency relates mainly to operational factors while absorption relates to financial issues. Avoidance of detrimental outcomes following cost increases will depend upon the ability of the industry to operate with reduced returns on operations. If returns are reduced substantially there may be an impact upon future investment decisions (this applies to new market entrants as well as existing producers). Lower returns will make future investment decisions less attractive and may lead to a reconsideration of current investments. Lower returns may also reduce the ability of the firms to raise finance (debt or equity capital) and increase the cost of finance. The impact on investment decisions may be international: it may deter inward direct investment from overseas or it may encourage UK firms to invest overseas in preference to the UK.

The affordability indicators which need to be examined can therefore be grouped into three categories: market (cost pass through), operational (cost pass back) and financial



(cost absorption). The assessment pursued here attempts to examine these indicators and the likelihood of detrimental outcomes on the basis of indicators of susceptibility.

## **C2.4 Defining affordability indicators**

An operational definition of sector affordability is the ability of the industry sector to absorb, pass through or pass back the costs of pollution control without jeopardising its short or long term prospects. This section aims to identify practical indicators of whether or not each of these three strategies is viable.

### **C2.4.1 Market indicators (cost pass through)**

Market indicators relate to the ability of the sector to pass through any impacts of BATNEEC application to final consumers. The outcomes will depend upon issues of competition in the market and conditions of final demand (availability of substitutes etc.). Indicators of interest are:

- **price strategies.** Pricing strategies can be a good indicator of the market conditions in which a sector operates (e.g. the impact of raw material and energy prices on operating costs and product prices etc.);
- **level of market protection.** Patents, economies of scale, transport costs, product differentiation, regulation etc. are important sources of market protection;
- **foreign competition.** Companies which operate the IPC process may sell into markets which have different levels of foreign competition. The effectiveness of pass through strategies will depend in part on the international dimension of the market. Foreign competitors may be put at a competitive advantage through the application of BATNEEC for UK operators.

### **C2.4.2 Operational indicators (cost pass back)**

Operational indicators will include such aspects as the scope for efficiency savings through changes to operating conditions etc.; these may be represented by:

- **asset turnover** - a measure of the efficiency of the company in generating sales from existing assets;
- **sales efficiency** - sales/employees - a measure of the relative efficiency of companies;
- **net income efficiency (NIEF)** - net income/employees - a measure of the relative efficiency in terms of contribution to profit.

### **C2.4.3 Financial indicators (absorption)**

The financial health of a sector, i.e its ability to absorb cost increases, is commonly measured in terms of financial ratios. Ratios are used because of the obvious need for standardisation across sectors with different characteristics. Financial ratios of interest are:

- gearing/leverage - net worth of company divided by its total debt;
- current ratio - current assets divided by current liabilities;
- return on sales - net income (pre tax profit) divided by sales;
- return on capital - net income divided by capital employed.

The financial indicators explored give an indication of both short term health (current ratio) and long term health (leverage) as well as financial performance (return on capital).

### **C2.4.4 Impact on Small and Medium Enterprises (SMEs)**

Overlaying all of these indicators is the issue of differential impact by company size. Many of the size issues can be dealt with at the level of NEEC application. However, there are broader issues regarding the impact on small and medium sized enterprises (SMEs). SMEs are often singled out for specific attention particularly in relation to environmental regulation because of the potential for them to be disproportionately affected.

Some of the principal reasons why SMEs should be considered in more depth are summarised below:

- *reactivity* - small firms tend to react to rather than anticipate regulatory and market change leaving them susceptible to external forces. Larger firms, alternatively, are often able to anticipate and pre-empt future change. The actions of industry trade associations can offset this difficulty to some degree;
- *skills shortages* - narrower operating activities often mean SMEs lack some of the skills and broad experience necessary to implement regulations cost effectively. Often this means they need to buy in skills from the outside at a significant premium;
- *capital constrained* - smaller firms are often capital constrained in that they face higher financing charges and have limited access to internal resources for funding;
- *product dependence* - small firms often depend on a limited range of products which means the impact of regulation tends to be more concentrated than for large firms.

## **C2.5 Assessment of Sector Affordability - Sector Overview**

### **C2.5.1 Introduction**

Analysis of the line of business of the companies reveals that there is a huge range of activities being undertaken by the companies operating the processes of interest. The only common feature that many of these companies have is that they own and operate a process for the manufacture of speciality organic chemicals. For some companies this is the ultimate function of the business operations, for others the chemicals produced are simply a stage in a further production process.

To undertake an affordability assessment for each and every market in which the companies operate would be time-consuming and of limited value given the small number of companies in some sectors. For the purposes of this assessment the majority of consideration is given to those companies mainly engaged in speciality organic chemicals manufacture. It is assumed that by analysing the economic factors affecting these companies the major issues affecting all companies who have an authorisation will be highlighted. Practically the stand-alone operators can be thought of as representing examples of the constituent processes operated by more integrated operations. The stand-alone companies, however, better highlight the financial and economic issues involved.

This section begins with a market overview for the speciality organic chemicals sector in the UK, examining industry characteristics, and recent UK performance. Section C2.5.2 contains a detailed description of the main markets for products. Section C2.5.3 discusses recent UK performance, while Section C2.5.4 discusses the markets for speciality chemicals.

### **C2.5.2 Chemical Sector Market Overview**

The organic speciality chemicals sector, as defined by the Department of Trade and Industry, is part of the larger UK chemicals sector, which is both its main supplier of raw materials (basic chemical products and feedstocks) and the main purchaser of its output (pharmaceuticals, agrochemical etc.). The UK chemical sector represents a large part of the UK economy accounting for almost 10% of the UK's gross domestic product earned by the production industries (ONS (1997) Blue Book).

#### **Industry characteristics**

The specialised organic chemicals industry has two main types of business: the custom synthesis of intermediate products on a contract or toll basis and the supply of own products. Suppliers operating in this industry are either SMEs, small divisions of larger companies or in-house divisions supplying other functions within the same company.

The number of stand alone operations has been estimated as approximately 150 (JEMU 1996). A third or so of these belong to the industry association SOCSA (Specialised Organic Chemicals Sector Association). The majority of these companies

sell their output to a small number (40 to 50) of purchasing companies. Major geographical concentrations exist in the M62 corridor, the West Midlands and Teesside.

In the main the divisional and in house operators conduct business like stand alone operators and are often, therefore, separate cost centres, although published financial data do not reflect this distinction. Product values range from £4/kg upwards and some products can reach the £20/kg plus range. The range of product volumes is estimated to be between 500g-1 kg (for lab chemicals) to 900 to 1000 tonnes at the top end. Anything above 1000 tonnes per annum is more likely to be undertaken by commodity organic chemical producers.

Investment and growth tend to be step wise as smooth growth from small to large is not generally possible. Mergers and acquisitions are therefore important vehicles for company growth (e.g. Ciba Specialities recent acquisition of Allied Colloids). Joint venture projects are also common, particularly in international markets. Growth in stages from 1 to 10 tonnes pa and from 10 to 100 tonnes per annum are generally achieved through acquisitions rather than new site investment or major extensions to existing sites. While merger and acquisition activity is rapid, it is reported (Tovey 1994) that since the 1980s there have been perhaps less than 20 new green or brown field sites in the UK. Even the brownfield sites tend to be additional processes at an existing operation.

The potential product output from these companies is immense. Chemical abstracts lists some 12 million chemicals that could in theory be produced. The majority of these chemicals are specialised organics. Within this range perhaps no more than 100 000 to 200 000 could be classed as being commonly traded. There has, however, been a trend towards product rationalisation within the industry which has even extended to customer streamlining. Niche marketing is also common.

The UK industry structure is unique in comparison to other countries because of the importance of relatively small stand alone producers. Major competitors (Germany, Switzerland and the USA) are far more reliant on up and downstream integrated businesses.

Customers of the sector are heavily concentrated in the most industrialised nations. The success of companies often depends upon the competitiveness and marketing ability of the companies to which it sells products. Most business is generated when new products are introduced by a customer or up-stream division of an in house operation. Product innovation by customers is of primary importance in determining sector growth. The main uses of products can be classified as<sup>1</sup>:

- pharmaceutical intermediates;
- agrochemical intermediates and ingredients;
- aroma and flavour chemicals;
- dye intermediates and pigment intermediates;

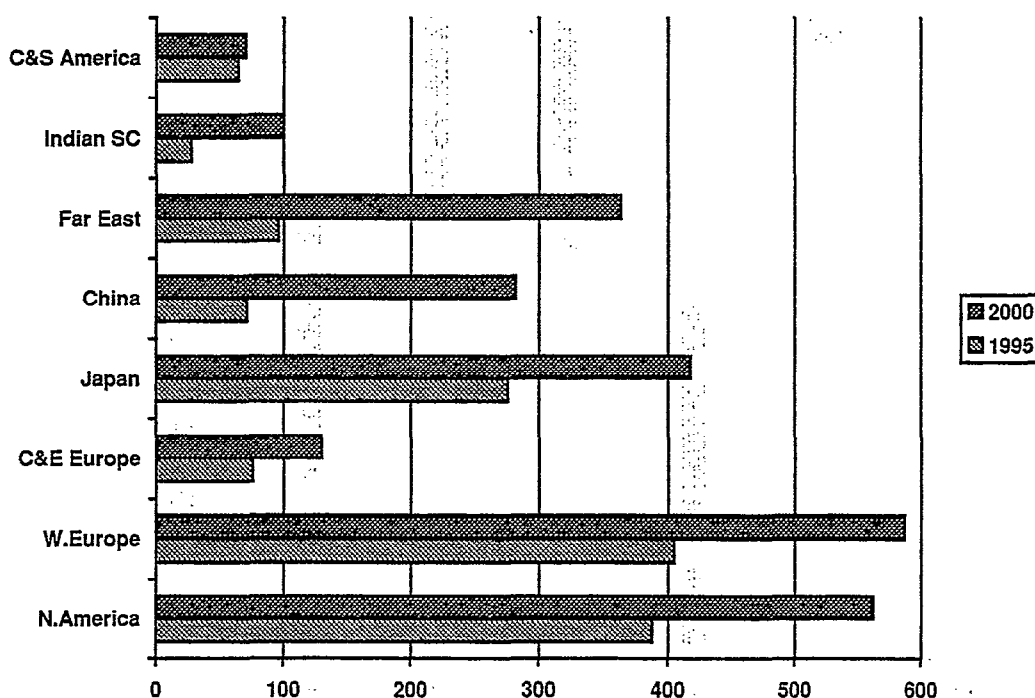
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<sup>1</sup> From Tovey (1994)

- organic biocides;
- organic flame retardents and intermediates;
- fuel additives;
- photographic chemicals;
- food additives (organic preservatives);
- detergent intermediates and ingredients;
- rubber chemicals;
- catalysts;
- plastics additives (organo-metallic);
- mining chemicals;
- leather processing chemicals.

The market for products is global and will remain so given the high value of products. (low relative importance of transport costs) and reductions in barriers to trade. Global market growth has been faster than the general growth in economic activity but the market is now maturing.

The market is concentrated in the US which in 1991 purchased 37% of the total global output of the speciality chemicals sector valued at \$42bn, i.e. \$15.5bn of consumption. The global markets have some notable characteristics. For example, the US market is large mainly because of the size of the rest of its economy. France has a large agrochemical demand because of its large (subsidised) farming industry. Figure C2 summarises the relative size of the world market for the chemical industry in general.



Source: CIA (1997)

Figure C2 Main Chemical Markets Estimated and Forecast Size (US \$b)

As can be seen all markets are expected to increase substantially with the largest growth in China and the Far East and on the Indian subcontinent. China in particular stands out as a growth sector. China currently has a push on speciality chemicals production as part of its ninth five year plan. The picture regarding the growth in consumption is mirrored by expected patterns of production growth on the global stage. It should be noted that these forecasts were made before the recent difficulties in Far East markets, and it is too early to predict their implications for the sector.

Pharmaceutical intermediates have grown faster than other product groups. Growth rates relative to the growth of the economy in general for the main product or market areas are given in the following table.

**Table C3 Growth rates for market sectors 1993-2000 (Tovey 1994)**

Market segment	Growth rate relative to growth in economic activity (%)
Pharmaceutical intermediates	+2.5
Agrochemical intermediates	-3.0
Dye stuff intermediates	-0.5
Aroma chemicals	+1.5

Companies with a high concentration of agrochemical intermediates in the product portfolio are therefore facing a contraction in output (assuming GDP growth of 2 to 2.5% per annum).

It should be noted that because of the structure of producers, account needs to be taken of the relative proportions of captive and outsourced demand. Captive demand is effectively that demand sourced to in-house operators. Captive demand is generally between 40 and 60% and is highest in the dyestuff and agrochemical intermediate sectors. Outsourcing is increasing in most markets although it is relatively stable in the pharmaceutical sector. The major trends in the pharmaceutical sector has been the series of drug-chemical demergers and, more recently, an increase in merger/take-over activity and the subsequent concentration of activity into fewer, larger companies.

### **C2.5.3 UK performance**

The chemical industry in the UK is one of the best performing sectors. A recent report (Insight 1997) places the chemicals and plastics industry as 2nd in the UK in terms of profitability (11.2% compared to a UK industry average of 6.1%) and ranked first in terms of the return on capital (27.5% compared to a UK industry average of 13.8%). The report suggests recent factors contributing to this performance include a general recovery in prices which were previously depressed and the benefits of a series of recent company restructuring. Companies with an emphasis on pharmaceuticals and niche speciality chemicals are also reported to have fared better than those which are commodity based.

Overall performance of the UK chemical industry is reflected in the speciality organics chemicals sector. The following table (Table C4), drawing on Tovey 1994, summarises a series of performance statistics for the UK sector. Although this information is slightly dated it is the most up to date information currently available and is used to illustrate trends.

The indices of production show the extent to which the growth in specialised organics has outstripped that of the chemical industry as a whole. This is reflected in the UK's share of world output which has increased from the 3-4% level in the 1970s to 7-8% for the 1980s.

As the figures for the standardised balance (the trade surplus or deficit divided by the total traded volume) show there has been a significant improvement from a small deficit in the 1970s to a large surplus.

R&D expenditures tend to be low in the stand alone specialised organics industry because most companies do not research and register new products in house. R&D expenditures, therefore are more comparable to general industry than the rest of the chemicals sector. R&D expenditures in the pharmaceuticals sector is of course much higher. The low R&D levels in the speciality organic chemicals sector may partly reflect the impact of the Notification of New Substances (NONS) regulations 1993. These provide an incentive for in house research and development relative to stand alone operations. The cost of a NONS application is estimated as £100 000 per chemical (Tovey 1994) and many applications will not result in a product being marketed.

As noted previously it is often not possible to determine the profitability of in-house specialised organics units within larger companies. Tovey examined the profitability of dedicated specialised organics companies which have the majority of their manufacturing in the UK. As can be seen profitability has varied considerably from year to year with a high of 15.4% and a low of 5.2%. The low profitability in 1990 and 1991 is a reflection of both the recession, large capital outlays and the impact of environmental improvement. It should be noted that profitability increased back to normal levels thereafter. A comparison of return on capital and other key business ratios, with industry and sub-sector averages is provided in Section C2.6.3.

In terms of productivity, value added per employee has been steadily increasing and in constant price terms increased three times between 1982 and 1992.

#### **C2.5.4 Industry linkages**

The input output data for the UK can be used to identify linkages up and down the production chain. Table C5 shows a break down of total demand for UK output from SIC (1980) classifications which correspond most closely to the IPC sector.

**Table C4 Recent performance indicators of the speciality organic chemicals sector**

Performance indicator	1970	1975	1980	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
<b>Output growth:(1985=100)</b>														
- specialised organics	n/a	48	93	n/a	n/a	n/a	100	n/a	n/a	218	n/a	221	n/a	253
- chemical industry	n/a	78	97	n/a	n/a	n/a	100	n/a	n/a	112	n/a	111	n/a	110
<b>UK share of world output</b>	3%	4%	8%	n/a	n/a	n/a	4.5%	n/a	n/a	8%	n/a	7%	n/a	n/a
<b>Trade balance</b>														
Exports (£m)	85	247	524	n/a	n/a	n/a	1150	n/a	n/a	1463	n/a	1694	n/a	2003
Imports (£m)	93	261	442	n/a	n/a	n/a	1060	n/a	n/a	1194	n/a	1289	n/a	1407
Standardised balance	-0.045	-0.027	0.082	n/a	n/a	n/a	0.041	n/a	n/a	0.101	n/a	0.136	n/a	0.175
<b>R and D intensity (% sales)</b>														
Specialised organics %	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.83	0.97	1.44
All chemicals	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	4.03
All industry	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	1.55
<b>Profitability (Return on Capital Employed)</b>														
Speciality chemicals	n/a	n/a	n/a	11.2	12.6	15.4	14.5	13.3	14.8	12.1	10.7	7.6	5.2	15.2
<b>Value added per employee £000</b>				6.1	8.5	12.2	12.4	12.9	14.9	15.1	15.1	15.1	14.1	18.4



**Table C5 Purchases of domestically provided output £m (% total)**

Purchasing Sector	Speciality Chemicals	
	£m	%
Industry	2474	51%
Consumers	180	4%
Government	49	1%
Exports	2172	44%
TOTAL	4893	100%

Source: UK Input Output tables, 1990, CSO. Note table ignores gross domestic fixed capital formation and stocks as these are very small (less than 1%).

For speciality chemicals, the table shows the importance of intermediate trade (purchase of speciality chemicals by industry for the production of final consumption goods). No less than 51% of the output of the speciality chemicals sector is purchased by industry, compared to only 4% which is sold directly to final consumers. This picture is broadly similar across the other related sectors. The importance of the export market for speciality chemicals is also demonstrated (44% of all UK output is purchased by overseas companies or final consumers). Government consumption of speciality chemicals products is comparatively low (1%).

The input output tables also identify the most important industry sectors purchasing the output of these sectors. For speciality chemicals the picture is one of highly dispersed demand throughout the economy: Only three sectors purchase 5% or more of the output, these being the "agriculture and horticulture" (19%) and "soap and toilet preparation" (6%) and "synthetic resins etc." (5%) industries. The sector is not a large user of its own products, purchasing only 3% of its own output.

In terms of backward linkages the following table (Table C6) shows the sales of goods and services to the sector:

**Table C6 Sales of goods and services to the speciality chemicals sector £m (% total)**

	Speciality Chemicals	
	£m	%
Sales to sector		
Other industry	1631	35%
Imports	970	21%
Taxes less subsidies	79	2%
Labour	928	20%
Profit	1065	23%
Total inputs	4673	100%

Source: UK Input Output tables, 1990, CSO Note sales by final demand.

Within the national accounts framework purchases by sectors include goods and services from suppliers but also treat the payment to employees and profits as returns for labour and capital “inputs”.

For the sectors the largest input to the production process is intermediate goods and services from other industries (35%). Imports are large, making up 21% of all inputs. Excluding taxes, labour and profit however, imports represent 37% of inputs demonstrating the high dependency of materials and services sourced from abroad.

Organic chemicals is the largest supplier of inputs to the speciality chemicals sector (supplying 15% of all inputs from UK industry). The next largest supplier of inputs is the wholesale distribution (of chemicals) sector (12%) followed by the inorganic chemicals sector (6%). Electricity accounts for 5% of UK industry sales to the sector.

### C2.5.5 Chemical Sector - Inward and Outward Direct Investment

The international dimension of the market for speciality chemicals has been noted above. One result of this is large scale ownership of assets in foreign companies and investment in the UK by foreign firms. Data are collected on the inward and outward direct investment flows and stocks for the UK. Direct investment covers the money invested in a related concern by a parent company. Thus outward direct investment is a flow of funds out of the country from the UK chemical industry to companies overseas. It is not necessarily related to capital investment in the overseas subsidiary. To qualify as a subsidiary the UK parent company must have at least a 20% stake in the assets of the company. The following table (Table C7) summarises the net book value of the assets owned overseas by UK companies, the earnings on those assets and the associated investment. The net book value relates to the total value of assets operated by the foreign affiliates (not just that part owned by the UK company).

**Table C7 Outward Direct Investment Characteristics (UK Chemical Industry) 1995 £bn**

Area	Net book value	Earnings	Investment
EU	4.5	0.9	1.5
N America	4.9	1.4	3.8
Asia	4.0	0.7	0.4
Other	3.6	0.8	0.1
Total	17.0	3.8	5.8

Source: ONS (1995) MA4 Overseas Direct Investment

The total value of chemical industry assets which the UK has a stake in overseas is therefore almost £17bn. These assets are fairly evenly spread across the globe, although the largest single share is in North America. In 1995 earnings on these investments were £3.8bn (the majority from enterprises operating in the USA).

Investments were higher at £5.8bn. The importance of outward direct investment is that it is often a vehicle for UK companies to sell their products in foreign markets.

It should be noted that the ratio of earnings to the value of assets invested is approximately 21% - similar to levels of return experienced in the home market. However, as the net book value exceeds the level of actual UK investment by some margin this would suggest that the return on investment is actually higher than 21%. This would suggest therefore that at present investing overseas is, in aggregate, probably more attractive than investing at home.

The level of inward direct investment partly reflects the competitiveness of the UK sector and its long-term prospects. Inward investment and earnings are approximately of equal value. Inward direct investment is a flow of funds into the UK by foreign based companies owning at least 20% of the UK company. The following table (Table C8 summarises the position in terms of inward investment.

**Table C8 Inward Direct Investment Characteristics (UK chemicals industry) 1995 £bn**

Area	Net book value	Earnings	Investment
EU	0.6	0.05	-0.03
N America	3.6	0.5	0.5
Asia	-	-	-
Other	1.0	0.03	-0.1
Total	5.2	0.6	0.4

Source: ONS (1995) MA4 Overseas Direct Investment

The total value of UK chemical industry assets in which overseas companies have a stake is therefore over £5bn. Much smaller than the value of assets in which the UK has a stake overseas. The return to foreign asset holders on investment in UK chemical industry assets, therefore, is approximately 11% - much lower than the return gained by UK companies from foreign assets. It should be noted, however, that the net book value is likely to overstate the actual level of investment and hence the actual return is likely to be higher.

The global ownership of assets is an important consideration for the assessment of affordability. Cost increases for UK based operations may lead to a reduction of inward investment and an increase in outward investment. A comparison of return on UK assets to foreign investors with returns to UK investors in foreign assets suggests a lower return on UK assets than UK companies are receiving from foreign investment activities. Cost increases, therefore, as a result of additional pollution abatement expenditure may exacerbate this situation.

## **C2.5.6 Market Analysis**

The economic assessment needs to take account of the conditions in the markets for speciality chemical products. The markets can be classified into a number of broad product groups.

### **Pharmaceutical Intermediates**

The market applications for speciality chemicals pharmaceuticals intermediates are diverse with a large number of potential customers. The largest single product accounts for 29% of all sales.

The majority of demand is concentrated in Western Europe and North America. Although a very competitive market with pressure on margins from health care systems, quality, reliability and flexibility are generally considered more important than price factors. Many ethical drugs manufacturers will keep to the same suppliers throughout the life cycle of the drug. This practice may be associated in many circumstances with the US FDA requirements. Large proportions of demand are satisfied by in-house units of pharmaceutical manufacturers, this is particularly true for Japan, N. America and France.

Business is largely dependent upon new product innovation. Analysts do not believe the product pipeline is in danger of drying up. Regulatory control means that products are costly and time consuming to develop. Development times of 13 years and costs of £100M per product are common.

It is estimated that there are over 3000 active ingredients being produced for the market globally. Competition from Eastern Europe and developing countries is intensifying. Many of the larger chemical groups invested heavily in the 1980's on dedicated plants to supply the growing market for intermediates. There has however been a notable reverse in this trend, with increasing emphasis on out sourcing.

The performance of UK suppliers of pharmaceutical intermediates is closely tied to new technological developments (e.g. chiral compounds) and the health of the UK pharmaceuticals sector. There are threats to this sector, notably from the expiry of a number of important patents, and the push for cost effectiveness in the health sector.

### **Agrochemical Intermediates**

The products for which agrochemical intermediates are required may be classified as:

- herbicides;
- insecticides;
- fungicides.

Herbicides is the most important category. The sector develops "active ingredients" which are used in finished products (containing one or more active ingredients) purchased by the agricultural sector.

Typical finished products have a world-wide production volume of a hundred to a few hundred tonnes. There is a constant pressure to reduce manufacturing costs through better processes and technologies. Agricultural systems are limiting market growth in Europe. The most important other markets are N. America and the Far East. UK production is very export orientated, with exports almost the same size as the UK market in 1994.

Annual growth is predicted to decline world-wide by 3% compared to general economic activity growth (Tovey 1994). The main impetus is environmental reform for agricultural policies. General trends identified are:

- declining market share for older products;
- an increase in post emergent products;
- increasing emphasis on higher activity lower volume products.

This last factor means an increasing requirements for active ingredients.

The market in the UK is dominated by in-house production by producers of agrochemical finished products, with a lower reliance on stand alone companies. In addition the UK is not a major source of raw materials for intermediate production. UK companies have also, historically, not been attracted to the sector because of the generally lower margins than in pharmaceuticals.

### **Pigment and dyestuff intermediates**

The markets for pigment and dyestuff intermediates is mature and is likely to grow slower than economic activity in general. Customers are concentrated into a few buyers. The market is affected by the shift in usage of dyestuffs east (Taiwan and South Korea) and increasing competition from India and China for some chemistries.

End users of intermediates are heavily concentrated in the textiles sector. Other end users include printing inks, plastics, paper surface coatings and leather.

Major restructuring of global operations has already taken place, with European production now geared to supplying high quality dyes for high quality textiles. Much lower value production has moved to the Far East. Many UK dyestuff manufacturers still make low value products for in-house use but do not compete on the open market. There is a risk, therefore that further cost increases would lead these companies to contract out to foreign firms as with most other low value products.

### **Fluorescent brightening agents (FBAs)**

FBAs are used in detergents, textiles, paper and plastics. In the detergents and textile markets the use of FBAs is closely linked since the use of FBAs in detergents in effect replenishes FBAs lost from fabrics during the washing wear cycle.

Supply is concentrated in a few companies, and there is a general switch in demand from the developed to the developing nations. Production is concentrated in the USA and Europe, with Europe supplying the bulk of non North American demand.

The UK has a relatively large share of world production. There is competition from “environment friendly” products not containing FBAs and from recycled paper.

### **Biocides**

Biocides kill micro-organisms. End users include wood treatment, disinfectants and sanitisers. Customers tend to be end users or formulators. The UK has one of the largest manufacturing bases in the EU. However, in many cases the biocide businesses are small parts of much larger companies.

### **Food additives**

The main organic additives are preservatives and vitamins. Vitamins, however, are usually treated as pharmaceutical products. The market is generally mature in the developed world and is likely to keep track with growth in general economic activity. The drive for healthy foods, particularly low sodium products, creates a demand for new additives.

The backlash against “E numbers” caused a decline in demand in late 1980s, from which the market has generally recovered. Few companies in the UK manufacture preservatives.

### **Aroma Chemicals**

Aroma chemicals are chemicals which when blended and added to consumer products impart a fragrance or flavour. Fragrance composition uses include detergents, toilet soaps, fine fragrances, toiletries and household cleaners. The market for aroma chemicals is concentrated in the developed world. Growth is greater than the growth in general economic activity.

Suppliers tend to be either perfumery companies with in-house intermediates manufacture or specialist manufacturers who may be back integrated.

Perfumery companies have certain advantages in the market through their understanding of the specifications of aroma chemicals required to meet perfumers requirements.

### **Plastic additives**

Plastic additives perform a number of functions, including heat and light stabilisers. Heat stabilisers inhibit oxidation while light stabilisers inhibit weathering in plastics. Light stabilisers are widely used for many plastics, heat stabilisers are dependent upon the PVC market. Customers are generally formulators of master batches for sale to plastics processors.

All markets are heavily influenced by the pressure put on the plastics industry by environmentalists.

## **Antioxidants**

Antioxidants prevent oxidation. The main end users are for additives to plastics, lubricants (motor oils) and rubber, although they are also used in toilet soaps. The market is characterised by a diverse range of low value products. The market is mature and there is little manufacture in the UK. The relatively low value of antioxidants means UK producers are not attracted to the UK market and consequently most domestic demand is met through imports.

## **Flame retardants**

Flame retardants find uses in plastics and textile applications where product safety requirements are high. The main markets are in construction, electricals and furniture making.

Demand is heavily influenced by safety legislation and hence is concentrated in the developed nations. Demand growth is expected to be higher than the growth in economic activity. New markets will be created as standards for flammability widen through the world.

## **C2.6 Indicators of Affordability**

This section presents an analysis of the affordability indicators. Broad level and detailed sub-sector analysis has been undertaken.

This analysis draws on a range of information sources but principally:

- general data relating to the UK as a whole (UK Ltd);
- general data relating to UK manufacturing enterprises;
- general data on related sub-sectors of the economy;
- specific data on the companies in the sector that have an IPC authorisation.

Information on the first three categories is summarised in Table C9 which shows market, operational and financial data for UK enterprises as a whole, the UK's manufacturing sector and a number of industry sub sectors closely related to the companies with an IPC authorisation.

**Table C9 Financial and economic data for related sector**

Financial indicator	UK Ltd	Manuf	Agri chem manuf	Chemical product manuf	Paint, varnish and allied products	Drug manufact	Industrial organic chemical manuf	Pharma goods wholesale	Rubber and plastic product manuf	Toiletries, perfumes and cosmetics	Plastics/synthetic fibre manuf	Converted paper product manuf	Chemical and allied product wholesale
Number of companies	372,871	68,084	168	516	305	509	197	1,036	4,961	759	315	1,049	1,535
<i>Market data</i>													
Profit margin upper	14%	9%	11%	9%	8%	13%	11%	7%	8%	10%	9%	8%	6%
Profit margin median	4%	4%	4%	5%	3%	6%	6%	2%	4%	4%	5%	4%	2%
Profit margin low	-1%	0%	0%	1%	1%	1%	2%	0%	0%	0%	1%	1%	0%
% change over 1993	46%	40%	133%	14%	-15%	20%	26%	40%	9%	28%	57%	18%	14%
<i>Operational data</i>													
Asset turnover upper	3.15	2.48	1.99	2.16	1.90	1.90	2.23	3.45	2.74	2.37	2.05	2.35	3.15
Asset turnover median	1.88	1.75	1.49	1.65	1.61	1.22	1.62	2.36	1.76	1.66	1.57	1.71	2.35
Asset turnover low	0.91	1.22	1.06	1.21	1.14	0.84	1.16	1.49	1.28	1.14	1.20	1.27	1.63
% change over 1993	5%	4%	0%	0%	7%	-2%	4%	7%	3%	-5%	11%	5%	1%
NIEF upper £K	8	6	14	11	11	15	20	12	6	10	10	7	21
NIEF median £K	2	2	7	6	3	6	10	4	3	3	5	3	7
NIEF low £K	0	0	1	1	1	1	4	0	0	0	2	1	1
% change over 1993	83%	64%	421%	64%	10%	94%	12%	48%	39%	70%	112%	32%	92%



Financial indicator	UK Ltd	Manuf	Agri chem manuf	Chemical product manuf	Paint, varnish and allied products	Drug manufact	Industrial organic chemical manuf	Pharma goods wholesale	Rubber and plastic product manuf	Toiletries, perfumes and cosmetics	Plastics/ synthetic fibre manuf	Converted paper product manuf	Chemical and allied product wholesale
<i>Financial data</i>													
Gearing upper	0.09	0.39	0.53	0.47	0.53	0.22	0.34	0.04	0.58	0.18	0.65	0.71	0.54
Gearing median	1.22	1.10	1.56	1.42	1.41	0.92	0.96	1.59	1.58	1.25	1.80	2.04	2.31
Gearing low	4.18	3.80	3.35	3.61	3.64	2.49	2.79	5.05	3.77	3.45	3.76	4.86	6.04
% change over 1993	3%	0%	34%	12%	22%	4%	-11%	2%	-2%	-3%	2%	14%	10%
Current ratio upper	1.60	1.70	1.50	1.90	1.80	2.10	1.00	1.60	1.50	1.80	1.50	1.50	1.50
Current ratio median	1.10	0.90	1.10	1.30	1.30	1.40	1.30	1.20	1.10	1.20	1.20	1.10	1.20
Current ratio low	0.80	0.90	0.90	1.00	1.00	1.00	1.00	0.90	0.90	0.90	0.90	0.60	1.00
% change over 1993	0%	13%	10%	8%	0%	8%	8%	9%	0%	0%	0%	0%	9%
ROCE upper	48%	35%	29%	33%	30%	32%	35%	49%	33%	34%	30%	34%	51%
ROCE median	12%	13%	15%	15%	12%	14%	20%	15%	14%	14%	16%	14%	22%
ROCE low	-1%	0%	3%	2%	3%	2%	7%	1%	1%	2%	4%	3%	4%
% change over 1993	-6%	37%	80%	-3%	33%	38%	17%	30%	-11%	17%	63%	16%	36%
ROA upper	17%	14%	12%	14%	13%	16%	18%	15%	14%	14%	13%	13%	14%
ROA median	5%	6%	5%	8%	6%	7%	9%	5%	6%	5%	7%	6%	6%
ROA low	-1%	0%	1%	1%	1%	1%	3%	0%	0%	-1%	2%	1%	1%
% change over 1993	36%	38%	160%	27%	0%	28%	-1%	35%	9%	16%	38%	31%	30%

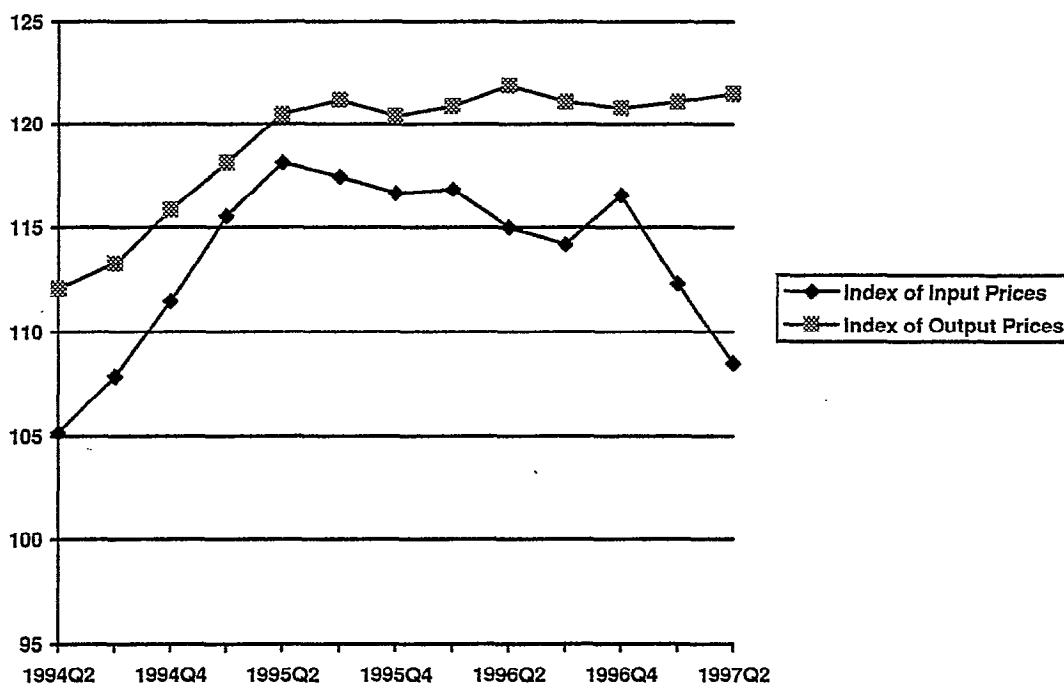
Note: See glossary for a detailed explanation of terms. NIEF - net income efficiency (profit/employee), ROCE - return on capital employed, ROA - return on assets.

### C2.6.1 Market Indicators

Market affordability indicators relate to the ability of the sector to pass through environmental costs to final consumers. Pricing, market access and foreign competition are all important aspects.

#### Pricing and market access

The recent trend in prices in the chemical sector has been one of the maintenance of output prices despite a rapid decline in input prices as shown in Figure C3



Source: ONS (1997) Sector Review, Chemicals, Rubber and Plastics

**Figure C3 Input and Output Price Indices - Chemicals**

The rapid escalation in prices between 1994 and 1995 was due mainly to an increase in the prices of ethylene and propylene (the basic raw materials for the industry as a whole). Prices of these products more than doubled between 1994 and 1995 because of a cyclical growth in demand and almost full capacity utilisation. The more recent decline in raw material prices is likely to be very beneficial to downstream chemical manufacturing operations like speciality chemicals. During 1994/95 escalating input prices lead to a squeeze on speciality chemical producers because of a resistance to price increases from customers. It is important to note how rapidly the economic outlook of the industry can alter. Investment plans may be based on timespans of 25 years, caution should therefore be exercised in using short term (6 month) fluctuations in input/output prices as a basis for decision making.

Within the sector the pricing strategy can be regarded as a modified full cost plus approach. Companies are asked to tender for the supply of a particular chemical product. Generally a customer will have a list of preferred suppliers. Each supplier will establish a supply cost and express a tender price on the basis of market information. This will include a consideration of:

- the importance of quality and specification of the delivered product and their ability relative to other potential suppliers to meet quality standards;
- the ability of the company relative to other suppliers to generate the required quantity of the chemical to a particular delivery date;
- the ability of foreign suppliers to respond etc.

On many products, particularly at the higher value end of the range there is considerable scope for using non-price elements of competition such as quality, reliability etc. to maintain a price premium over other suppliers. In addition the use of preferred lists of suppliers means there is an element of market protection as new suppliers will have to “prove themselves” to get on to the appropriate shortlists.

IPC authorisations within the sector may also have an effect on competition. The need to pre define outputs introduces a certain amount of rigidity into the system which mean that there may be delays in reacting to market opportunities. Envelope authorisations address this problem to a certain extent by extending the range of products that can be made by the process.

As noted above niche marketing is another important characteristic of the industry. The complexity of some of the techniques involved means there is a rationale for specialisation. Successful niche marketing will also increase the ability of cost pass through by reducing the effective number of competitors.

Long term contracting is another issue which introduces a level of market protection. For quality control purposes some customers may prefer long term contracts with suppliers. For example, in the pharmaceuticals sector such contracts may remain in place for the duration of the product's life time.

An assessment of the degree of market protection which is available can be obtained from a comparison of the profit margin displayed by the companies with IPC authorisations with other sectors in the economy. The higher the profit margin, other things being equal, the more market protection is available to the companies. Table C9 shows the median profit margin displayed by UK enterprises as a whole is 4%. The figure is broadly the same as the UK manufacturing sector. Across those sectors which correspond most closely with the sectors within which the companies with authorisations operate, profit margins vary between 2 and 6%.

The following table (Table C10) shows the profit margins earned by companies with IPC authorisations.

**Table C10 Profit margins of authorised companies**

Sector	Profit Margin %
All sectors	7
Basic pharmaceuticals	17
Food products	13
Other chemical products	7
Other organic basic chemicals	7
Paints etc.	3
Pesticides/agro-chemicals	7
Pulp and paper	11
Soap and detergents	3
Textiles	4
Other plastic/rubber products	6
Wholesaling	8

As the table shows, profit margins in the majority of cases are in excess of both the UK and manufacturing averages as well as for related sectors. The three notable exceptions are paints, soap and detergents, and textiles whose profit margins are lower by comparison. These data would appear to confirm the proposition that there is a degree of market protection in the sector.

The EC's review of the single market impact on the chemical sector confirms these characteristics: highlighting the importance of quality relative to price. In some cases, therefore there would appear to be evidence that cost pass through may be possible, particularly in light of falling input prices and the importance of non price output characteristics.

### **Foreign competition**

Within the chemicals sector intra EC trade flows are more important than trade with the rest of the world. Intra EC exports and imports were 64% of total exports and imports in 1993. This statistic illustrates the importance of geographical proximity in the trade. One of the main issues, related to foreign competition is the level of import penetration. Import penetration is the ratio of imports to apparent consumption. Growing levels of import penetration are indicative of susceptibility to foreign competition for UK producers.

The UK's main competitor nations are Germany, Switzerland and the USA. Japan although home to the second largest chemical market in the world tends not to be major international player despite a commitment expressed in the late 1980s to play a more international role. Outside the developed nations India, Korea, Taiwan and China are rapidly developing as competitors. While these countries tend to have lower environmental cost burdens, their innovative and technical expertise rival companies in

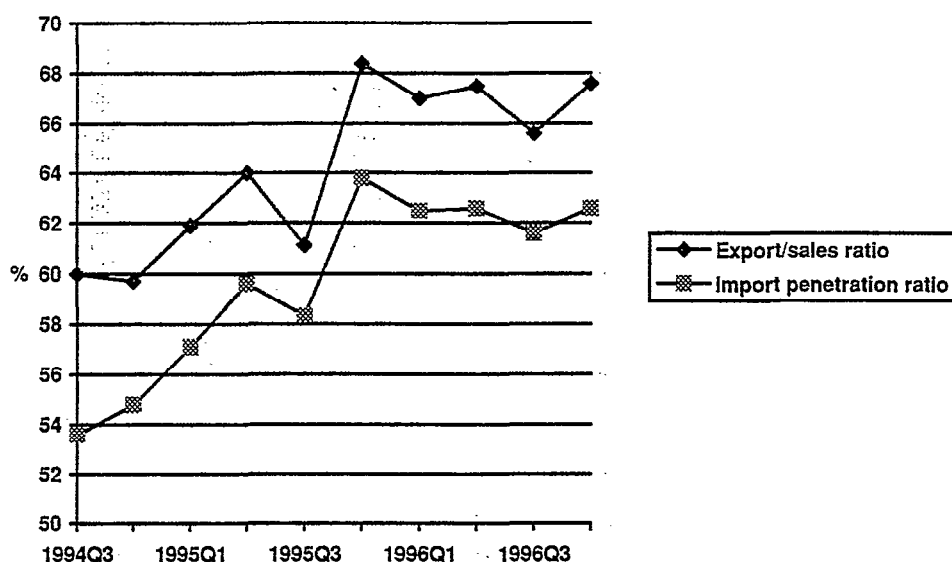
the developed world. They are therefore able to react to new product markets with quality outputs but with a lower cost base.

Companies operating in the UK benefit from one of the lowest tax bases of any of their international competitors. Approximate tax burdens on business as a proportion of GDP in a number of competitor countries is summarised below (HMSO Competitiveness White Paper 1996):

- France . . . 14%
- Italy . . . . 14%
- Japan . . . . 10%
- Germany . . 10%
- US . . . . . 7%
- UK . . . . . 7%

This tax burden includes corporation taxes, payroll taxes and employer's social security contributions.

Figure C4 shows recent experience of the UK chemicals sector as a whole in terms of import and export performance.



**Figure C4** Export/sales and import penetration ratios for the UK chemicals sector as a whole

As the diagram demonstrates there has been a generally increasing trend in the proportion of sector sales that are exported. In addition however, the upward trend on the import penetration ratio shows that an increasing proportion of UK demand is being met from imports. This picture is consistent with the general trend of globalisation in the market, and in particular the shift away from low value products in the UK.

The degree of foreign competition and export intensity varies from sector to sector. The following diagrams summarise recent experience with import penetration and the level of exports relative to sales.

Figures C5 and C6 provide a more detailed breakdown of export sales and import penetration ratios, respectively, for the sector.

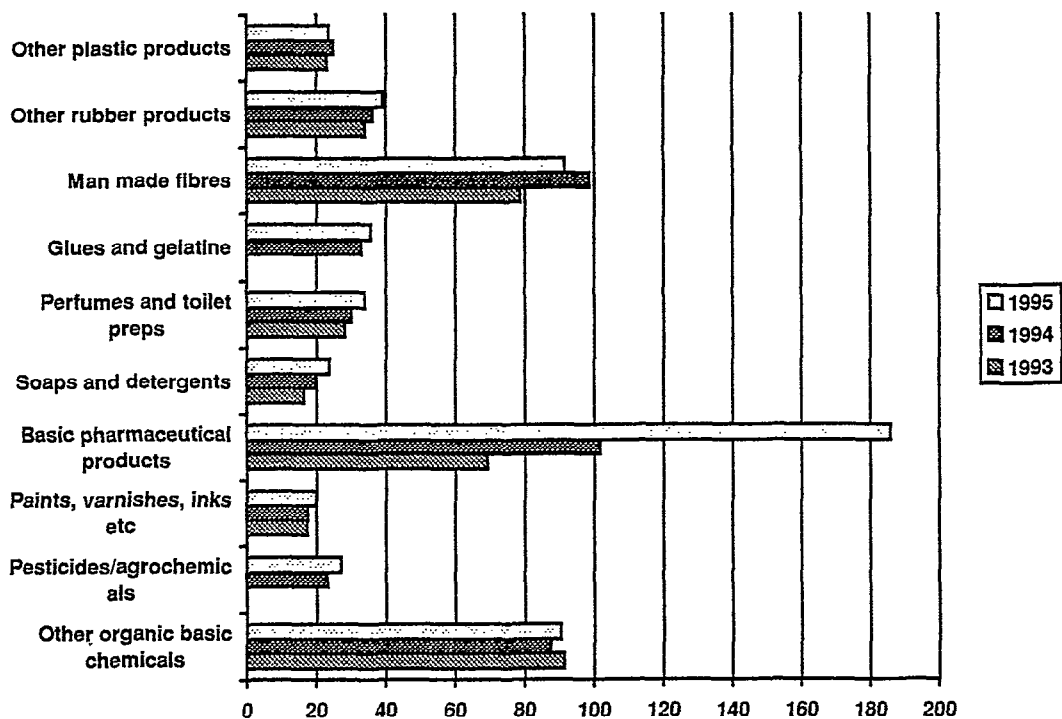
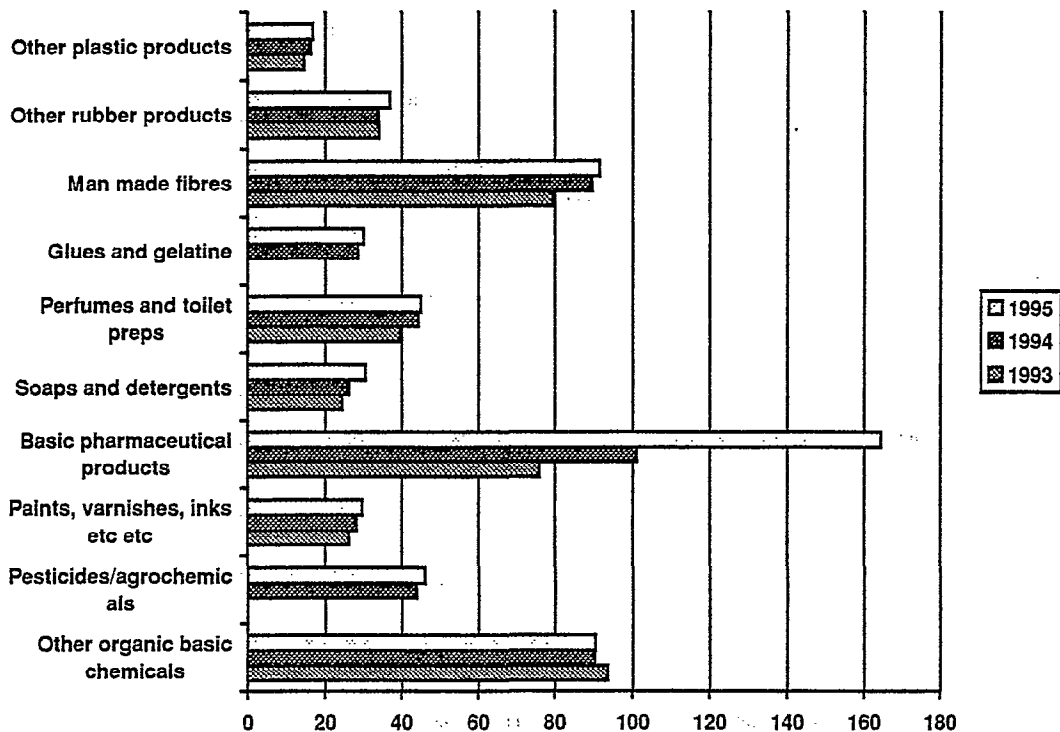


Figure C5 Import penetration ratios for selected sector 1993-1995



**Figure C6 Export sales ratios for selected sector 1993-1995**

In terms of import penetration the majority of sectors have experienced increased susceptibility to imports over the period 1993 to 1995. The largest increase has been in the basic pharmaceutical products sector. A number of sectors, however have seen relatively little change over the period - this is true of other organic basic chemicals, other rubber and plastic products and paints etc.

For exports the picture is much the same - pointing to the fact that although the UK is experiencing increased competition in some markets it is also performing well in export markets. The recent strength of sterling, however, may mean a deterioration in trade balances. Once again the picture is strongest for the basic pharmaceutical sector. One sector - other organic basic chemicals has seen declining exports over the period.

Given the importance of the global market it is important to examine the relative level of regulation in major competitor countries. Regulation itself needs to be considered together with the level of enforcement and many other factors. The important point in economic terms is the relative economic burden imposed by environmental control in the different competitor countries. Although on some aspects other countries may be more strict on others, it is considered that the level of environmental burden in the US, Germany, The Netherlands and the Scandinavian countries is approximately similar to that in the UK although in some circumstances it may be less tight. In Lower European countries regulation is, however, regarded to be less stringent; while the level of environmental control in developing and emerging nations is generally considered to be lower still.

In an analysis of the factors affecting the competitiveness of the UK chemicals sector (the example used was commodity polymers) in relation to VOC controls, a study for

the DTI reviewed the relative stringency of controls in the UK, Belgium, Germany and France. They concluded that controls in all countries with the exception of France were broadly consistent with EPA90. In France controls were thought to be less stringent, particularly for vent emissions.

From this limited information it is difficult to offer any robust conclusions regarding the relative levels of control. However, from the available evidence, the UK chemicals sector would appear to have amongst the highest environmental cost bases of its competitors.

It should be noted, however, that despite the existence of such a competitive disadvantage the UK chemicals sector has continued to perform strongly on international markets. A number of other factors potentially offset the susceptibility to foreign competition:

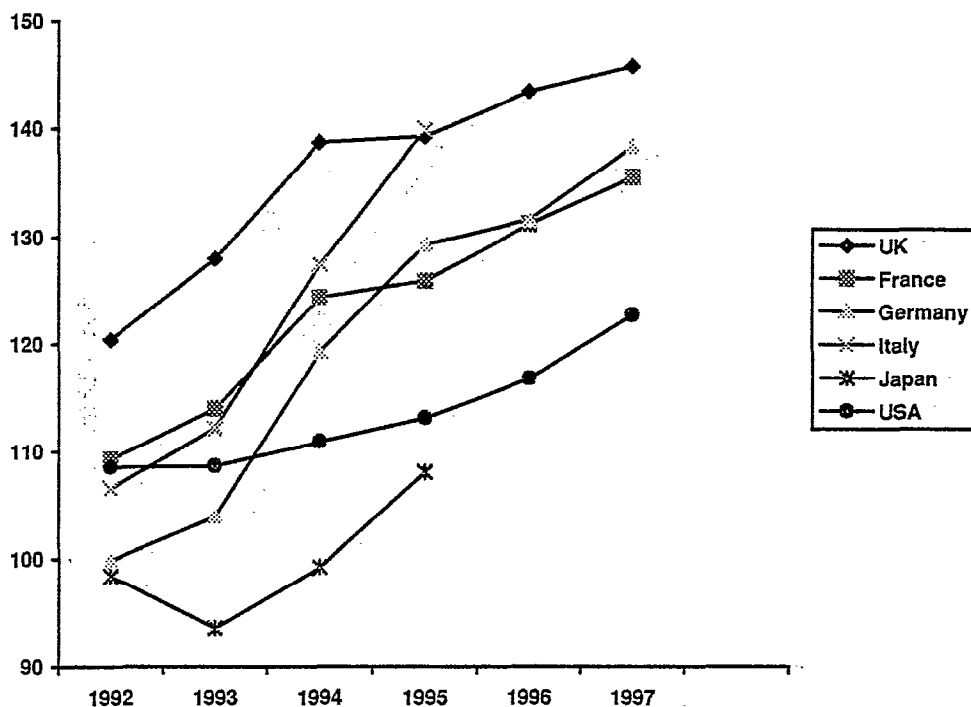
- US FDA approval system means in many respects a level playing field is created for all pharmaceutical companies selling into the US market;
- EU Pesticides Approval, Marketing and Use Directive. Similar to above, although less pronounced.

Although it should be noted that the systems are primarily driven by product use rather than their manufacture.

### **C2.6.2 Operational Indicators**

Figure C7 shows that productivity growth in the UK was one of the fastest of the major competitor countries between 1992 and 1994. Since then there has been a considerable slowing in the growth of productivity. A continuing decline in productivity growth would indicate little scope for cost pass back strategies.





Source: ONS (1997) Sector Review, Chemicals, Rubber and Plastic Products, Quarter 2 1997.

**Figure C7 Productivity Indices - Chemicals and Chemical Products**

Two measures of operational efficiency are available from the company data - asset turnover and net income efficiency (NIEF). As Table C9 shows asset turnover (sales/assets) for UK enterprises as a whole is 1.88. (i.e. £1.88 of sales per £ of money invested in assets). This figure is higher than manufacturing in general. For the related sector asset turnover rates range from 1.22 to 2.36 (see Table C7). The highest rate is in the pharmaceutical goods manufacture. The following table (Table C11) shows the rates of asset turnover for the sample of authorised companies.

**Table C11 Asset turnover of companies with an IPC authorisation in this sector**

Sector	Asset Turnover
All sectors	1.16
Basic pharmaceuticals	1.02
Food products	1.32
Other chemical products	1.06
Other organic basic chemicals	1.26
Paints etc.	1.35
Pesticides/agro-chemicals	1.03
Pulp and paper	1.02
Soap and detergents	1.93
Textiles	1.12
Other plastic/rubber products	2.10
Wholesaling	1.49

As the table shows, efficiency of the companies on this measure, is generally at the lower end of the range identified for comparable sectors and therefore there may be scope for efficiency improvements.

The second measure of efficiency is the net income efficiency (NIEF) or profit per employee. As Table C7 shows, profit per employee for UK enterprises as a whole was £2000 in 1995. The same figure applies to the manufacturing sector as a whole. By comparison the levels of profit earned per employee for the related sectors is considerably higher - ranging from £2000 to £10 000. This of course partly reflects the capital intensity of the industry relative to the UK as a whole. High levels of capital intensity mean that more output can be produced with fewer employees.

The levels of profit per employee in the companies with IPC authorisations is summarised in the following table (Table C12).

**Table C12 Net income efficiency of companies operating in the sector**

Sector	NIEF £'000
All sectors	16
Basic pharmaceuticals	26
Food products	4
Other chemical products	7
Other organic basic chemicals	21
Paints etc.	4
Pesticides/agro-chemicals	16
Pulp and paper	16
Soap and detergents	5
Textiles	17
Other plastic/rubber products	26
Wholesaling	21

Levels of profit per employee are considerably higher in a number of sectors - basic pharmaceuticals, other organic basic chemicals, other rubber and plastic products and wholesaling. By comparison food products and soap and detergents have much lower levels of efficiency on this measure.

The two measures of efficiency therefore present a contrasting picture. On the basis of asset turnover, the companies appear to be at the lower end of the range of efficiencies. On the basis of NIEF, however, the companies would appear to be more efficient than comparable sectors. This latter measure, however, may be unduly influenced by the capital intensity (the importance of capital in generating output relative to manpower) of the companies.

### **C2.6.3 Financial Indicators**

Analysis has been undertaken on a number of financial indicators including gearing, the current ratio, the return on capital employed and return on assets by industry sector.

#### **Gearing**

The gearing ratio shows the relationship between a company's total debt and its net worth or equity capital. For example if a company had a total debt of £500 000 and a worth of £1 000 000 then the gearing of the company is 0.5. Gearing is an important issue for companies. Optimal gearing is generally viewed as a trade off between the tax advantage of debt and the lender's increasing fear of bankruptcy which is associated with higher gearing. The tax advantage of debt stems from the fact that interest charges are made to the profit and loss account and therefore decrease the overall tax liability, whereas returns to the providers of equity finance (i.e. shareholders) are post tax. Hence from this point of view it is always preferable to finance investments through debt.

Gearing will have an impact on companies' ability to finance investment in pollution control and will also determine the costs of servicing finance. Companies with a high level of total debt are regarded as vulnerable in that they must meet interest commitments whether profits are made or not and may therefore be forced into short term measures (sales of assets) which may jeopardise the long term future of the company. The lower the proportion of net worth not owed in debt the less vulnerable the company as repayments to the owners of the assets (dividends on equity) do not need to be paid in any one year, although a low dividend payment record will also jeopardise future operations. The cost of capital for highly geared companies will, therefore, be proportionately higher.

Table C9 shows rates of gearing for UK enterprises, the manufacturing sector and sectors related to this study. Average rates of gearing are 1.22 for all UK enterprises and 1.10 for the manufacturing sector. In related sectors gearing rates range from 0.92 to 2.31. As can be seen rates of gearing in the related sectors are in general considerably higher than the average for manufacturing.

The following table (Table C13) summarises the average rates of gearing in the authorised companies.

**Table C13 Gearing rates of companies operating in the sector**

Sector	Gearing
All sectors	1.36
Basic pharmaceuticals	0.94
Food products	1.41
Other chemical products	1.39
Other organic basic chemicals	1.67
Paints etc.	1.65
Pesticides/agro-chemicals	1.35
Pulp and paper	1.29
Soap and detergents	1.52
Textiles	1.06
Other plastic/rubber products	1.33
Wholesaling	1.14

Gearing rates are generally similar to those found in related sectors. Relatively high rates of gearing are seen in the other organic basic chemicals sector and paints etc. sectors. However, even these rates are within the range of related sectors. Across all sectors 15% of companies have gearing greater than 2.00. This analysis would suggest that although high rates of debt may be a constraint on individual companies in general the sector is relatively well geared.

### **Current ratio**

The current ratio (CR), often called the liquidity ratio, is an indication of liquidity - the ability of the company to pay its immediate debts. The liquidity ratio is generally regarded as the best indicator of forthcoming bankruptcy. Theoretically a current ratio of 1:1 is required. However, given the low probability of a company facing demand for all current liabilities at the same time, a ratio of 0.7:1 is considered to be a rule of thumb for an acceptable current ratio. Companies with a CR of 0.7 could meet 70% of their short term liabilities almost immediately if asked to do so. A CR of less than 0.7 is considered to be unacceptable. A CR of greater than 0.7 is considered acceptable although high CRs can indicate a poor management of funds.

As Table C9 shows the current ratio for all UK enterprises is 1.10. This is higher than the average for the manufacturing sector (0.90). For the related sectors current ratios are generally the same as or above the average for the UK. This would suggest that these sectors are generally more liquid than the manufacturing sector as a whole.

The following table (Table C14) shows current ratios for the IPC sector.

**Table C14: Current ratios of companies operating in the sector.**

Sector	Current Ratio
All sectors	1.68
Basic pharmaceuticals	1.52
Food products	0.84
Other chemical products	1.72
Other organic basic chemicals	1.48
Paints etc.	2.57
Pesticides/agro-chemicals	1.35
Pulp and paper	1.36
Soap and detergents	1.44
Textiles	1.83
Other plastic/rubber products	1.78
Wholesaling	3.60

As the table shows, liquidity in these sectors is generally higher than for the related sectors and considerably higher than the averages for UK enterprises and the manufacturing sector. This high level of liquidity would suggest that in aggregate the sector does not have a liquidity problem. The exception here is for food products which has the lowest current ratio, although it is still in excess of the critical 0.7 level.

Further analysis of the data indicates that of all the companies for which financial data could be compiled (172) 14% had current ratios below 0.7. Hence a number of companies appear to have difficulties on the basis of current ratio's although this is not true of the sectors as a whole. The sectors with the greatest proportion of companies with current ratios less than 0.7 are food products (50%), manufacture of other organic basic chemicals (26%), paints etc. (34%), textiles (38%), other plastic and rubber products (17%) and wholesaling (17%).

### **Return on capital employed and return on assets employed**

Return on capital employed (ROCE) and return on assets (ROA) are measures of profitability. They aim to measure the amount of net income earned by the company through product sales in relation to the value of the capital (machines etc.) required to produce the output. Return on capital employed is generally higher than the return on assets as some assets are not "employed" e.g. intangible assets like customer goodwill. All other things being equal the company with the highest ROCE or ROA is the one which is most profitable. Profitability in this context is obviously a relative term. A company can have a small absolute level of profit but be more profitable (in terms of ROCE/ROA) than a company with a large absolute profit level.

The returns are also seen as important in determining investment. Each company will face a cost of capital (e.g. the interest on borrowed funds or the opportunity cost of internal funds) in employing capital. A good level of ROCE/ROA will obviously

encourage investment. The difference between the return and the cost of capital is an indicator of the desirability of the investment. This indicator is often termed the valuation ratio or Tobin's Q.

Table C9 shows that the average ROCE for UK enterprises as a whole is 12%. For ROA the figure is 5%. Returns in the manufacturing sector are slightly higher at 13% and 6% respectively. For the related sectors ROCE varies from 14% to 22%, while ROAs are in the range 5 to 9%, suggesting that the sectors are more profitable than the manufacturing sector as a whole. The following table shows ROCE and ROA averages for the companies with IPC authorisations.

**Table C15 ROCE and ROA of authorised companies**

Sector	ROCE %	ROA %
All sectors	19	8
Basic pharmaceuticals	23	15
Food products	40	17
Other chemical products	12	6
Other organic basic chemicals	19	9
Paints etc.	14	5
Pesticides/agro-chemicals	12	7
Pulp and paper	16	11
Soap and detergents	9	5
Textiles	28	5
Other plastic/rubber products	19	7
Wholesaling	9	10

Returns in the majority of sectors are higher than the comparable figures for the UK as a whole, for manufacturing and for the related sectors. This would suggest that the companies are on average more profitable than most.

## **C2.7 Simulated Cost Escalation Scenarios**

This section presents the results of an analysis to examine the impact of a number of scenarios for operating cost increases on the profitability of firms within the IPC sector. The financial data collected for the companies has been used to derive an estimate of operating expenditure (sales less profits). The operating expenditure estimate is an average over the two years of available data.

Two forms of analysis have been undertaken, both of which involve 1%, 2.5%, 5% and 10% operating cost increases. The first analysis looks at the number of firms whose return on capital falls below the sectoral average as a result of the cost escalation. The second looks at the number of firms whose return on capital falls below 15%.

This analysis is restricted to the issue of absorption of cost increases. No account is taken of other strategies - such as cost pass through or pass back. A fuller analysis would need to take account of impact on prices, demand, investment, gearing, profit margins and working capital. The choice of the cost increase scenarios, and the 15% benchmark for the second analysis is necessarily arbitrary but is likely to encompass the majority of real world cases.

### C2.7.1 Results of cost escalation scenarios

The cost increases, taken across the firms, may be thought of as funds available for investment in environmental improvements. The funds generated by the cost increases are:

Percentage cost increases	Funds raised across the whole sector
1	£50m
2.5	£140m
5	£270m
10	£540m

Tables C16 and C17 show the results of the cost escalation scenarios for the companies as a whole and the individual sub-sectors.

**Table C16 Percentage of companies with below average ROCE as a result of operating cost increases**

Sector	No of companies	% with ROCE less than sector average following cost increase				
		Base	1%	2.5%	5%	10%
Basic pharmaceutical products	17	65	65	65	65	82
Food products	2	50	50	100	100	100
Other chemical products	14	50	57	71	86	93
Other organic basic chemicals	29	59	62	76	79	97
Other plastic and rubber products	24	71	79	79	88	92
Paints, varnishes etc.	6	50	50	50	100	100
Pesticides and agro chemicals	3	67	67	67	100	100
Pulp and paper products	2	50	100	100	100	100
Soap and detergents	2	50	100	100	100	100
Textiles	7	71	71	71	71	100
Other manufacturing	18	67	72	72	78	89
Other	3	33	33	67	100	100
All sectors	130	62	68	74	82	92

As the table shows, of the 130 companies analysed 62% have ROCE less than the average (pointing to a skewed distribution). A small cost increase of 1% would lead to a small increase in the number of companies with below average ROCEs - an additional 6% or 8 companies in total. Moderate cost increases of 2.5% and 5% lead to a further 6% and 8% of companies having below average ROCE. Large cost increases (10%) would lead to 30% of companies (40 companies) seeing their ROCE fall below the industry average compared to the base situation.

The picture for individual sub-sectors is much more complicated. For a 1% cost many sectors do not see a change in the number of companies with below average ROCEs, this is true of basic pharmaceuticals, food products, paints, pesticides, textiles and other. Indeed a number of sectors do not see a significant change in the number of companies with below average ROCEs until high levels of additional costs. In the basic pharmaceutical sector for example, the number of companies experiencing below average ROCEs remains the same until cost increases of 10% are seen. Although it should be noted that high levels of ROCE are generally required in this sector because of the long product development times and riskiness of investment expenditures. The majority of sectors therefore would appear capable of absorbing small and moderate cost increases on the basis of the impact on the return on capital.

An alternative perspective is given by examining the impact of the cost increases on the number of companies having their ROCE fall below 15%. A 15% ROCE is to a large extent arbitrary and takes no account of the different risk profiles experienced by the companies which will tend to mean different acceptable rates of return for different sectors. However, 15% is chosen as the benchmark for this analysis as a broadly acceptable return on investment. The results of this analysis are shown in the following table (Table C17).

**Table C17 Percentage of companies with below average ROCE as a result of operating cost increases**

Sector	No of companies	% with ROCE less than 15% following cost increase				
		Base	1%	2.5%	5%	10%
Basic pharmaceutical products	17	24	35	53	59	65
Food products	2	0	0	0	0	100
Other chemical products	14	50	50	71	79	93
Other organic basic chemicals	29	38	48	52	59	79
Other plastic and rubber products	24	42	46	58	75	88
Paints, varnishes etc.	6	50	50	50	100	100
Pesticides and agro chemicals	3	67	67	67	100	100
Pulp and paper products	2	0	0	50	100	100
Soap and detergents	2	50	100	100	100	100
Textiles	7	71	71	71	71	86
Other manufacturing	18	67	67	72	72	83
Other	3	67	67	100	100	100
All sectors	130	46	52	62	72	85



The main differences between these results and those based on average ROCEs is the lower number of companies with ROCEs less than the benchmark in the base situation. Otherwise the results are broadly similar with small increases in cost leading to small changes in the number of companies experiencing ROCEs of less than 15%. Notable exceptions, however, are the basic pharmaceuticals and other organic basic chemicals sectors which were relatively insensitive to small cost increases on the average ROCE measure but see an extra 10% of companies with ROCEs falling below the benchmark of 15%. This would suggest both sectors have a grouping of companies whose ROCEs are close to the 15% benchmark level in the base situation.

## C2.8 Conclusions

The picture presented by this assessment of affordability is varied. This reflects the diversity of the companies operating within the IPC sector. Overall the concept of sector affordability as a useful tool for Inspectors in the practical application of BATNEEC would appear to be limited. However, the concept does have a much greater potential for use in strategic decision making.

The broad conclusions which can be drawn from the analysis of sector affordability are summarised below:

1. The market prospects for the sector covered are largely determined by the level of general economic activity. There are exceptions, however, notably the agricultural chemicals sector.
2. The markets in which the companies operate are global in nature and will be influenced by conditions in other countries, (notably the USA for product sales and the Far East for competition).
3. The prospects of the sectors depend upon new product innovation which in general is unlikely to be curtailed as economic growth proceeds.
4. The UK unlike other countries relies heavily on SMEs for a large proportion of activity in this sector.
5. The general conclusion from the market analysis is that the UK has already moved out of the low value end of the product market although there are still some in house producers operating at this level.
6. There are rigidities in the market which mean that price competition although important may not be fundamental in all markets suggesting some scope (on a case by case basis) for cost pass through. This is reflected in generally high levels of profit margins.
7. The returns available from investment in foreign markets appear to be higher than the return offered in the UK to foreign investors. Cost increases could worsen this situation.

8. The majority of sectors have witnessed increased import penetration and increased exports - possibly reflecting the globalisation of the market and the move away from low to high value products.
9. The rapid growth in productivity improvement has recently declined suggesting limited scope for cost pass back. A contrasting picture is given in terms of efficiency measures with asset turnover suggesting there is scope for efficiency gains, while net income efficiency suggests the scope is more limited.
10. The available evidence suggests the UK already has one of the highest levels of environmental cost base of its competitors.
11. Analysis of the gearing rates for the companies suggests the sector as a whole does not have a significant debt constraint, although this may be different for particular companies.
12. The majority of companies appear to be relatively liquid, although 14% of companies can be regarded as having an unacceptable liquidity position. These companies could face short term difficulties if required to invest heavily in pollution control.
13. Returns on capital are generally high both on the basis of the return on capital employed and the return on assets.
14. On the basis of simulated cost increases the majority of sectors would appear capable of absorbing small and moderate cost increases on the basis of the impact on the return on capital.

### **C3. NOT ENTAILING EXCESSIVE COST APPROACH**

#### **C3.1 Introduction**

This section draws on the methodology outlined in the Technical Guidance Note (TGN) E1 (HMSO 97a). The section begins with a brief précis of the methodology (Section C3.2), discusses the application of the methodology in the particular circumstances of the Organic Speciality Chemicals Sector (Section C3.3) and discusses some examples of the treatment of various important issues. Section C3.4 presents some generic information on pollution control costs and Section C3.5 discusses benchmark economic data to assist Inspectors in examining the supporting information provided by operators. Section C3.6 discusses a number of sources of information while Section C3.7 draws together the conclusions on the use of the NEEC approach.

## C3.2 General Issues

The basic principles of the methodology are adequately spelt out in the TGN E1. A number of points need to be made about this methodology from the outset:

- the methodology is one of examining the cost effectiveness of pollution control abatement rather than defining the net benefits or net costs.
- The methodology is concerned with the financial costs to the operator rather than the social costs of the BAT intervention.
- The methodology provides minimal guidance on price and demand effects.

Annex III provides a suggested method for incorporating the approach to NEEC into the economic assessment methodology. Guidance is given on where and when the information in the rest of this section will be useful to both operators and Inspectors during the assessment.

### C3.2.1 Stages in the methodology

The purpose of the methodology is to assess the costs of a number of options for pollution control investment and compare these to the environmental impacts to determine the most appropriate option.

Annex III identifies seven principle stages in the economic assessment. The stages begin in the situation where the operators preferred option is not the best environmental option. In these circumstances the full range of feasible options will need to be defined.

It is likely that the situations in which an assessment will be made will be:

- *retro fitting technology to existing plant.* This is where the existing plant is not due to be upgraded or machinery replaced within the next review period. In this case there may be a variety of potential options which need to be investigated including a "business as usual case" and a series of options. the business as usual case may or may not be the preferred option suggested by the Operator;
- *upgrading of existing plant.* This is where existing plant needs to be upgraded anyway and the question is whether to do it with a particular technology or not and any changes are solely driven by environmental considerations. In this case there will be no business as usual case as the plant will be upgraded in all situations;
- *new plant.* This is where an entire new investment in a plant is being considered. Once again there will be no business as usual case although there should be a preferred option and a series of alternatives.

In general, because of the complex nature of the sector's processes and its interactions with other processes and operations it is important that the NEEC assessment is defined so as to include all the processes impacted. Initially the limits of the assessment will need to be defined by the operator. All material impacts will need to be considered. The use of checklists of other processes' operations to identify those affected should be considered.

During this stage it is important that all possible options are considered, the preferred option or baseline case has been properly defined and spillover or feedback effects correctly identified.

Stages 3 and 4 address the costs to the operator of the various options. Costs of options need to be expressed in comparable terms. Annualisation of costs effectively allows comparison of options with different expenditure profiles on a consistent basis. Once annualised, costs of projects can be compared more directly. Inspectors should be aware, however, that particular profiles of cost can cause difficulty for firms in terms of their cash flow situation (liquidity). The control of cash flow and financing arrangements have become one of the most important aspects of running viable businesses. Lack of liquidity is one of the most reliable predictors of bankruptcy.

Annualisation of costs also requires the choice of a capital cost time horizon. The life time of the equipment specified by the operator needs careful interpretation and should, where possible, be verifiable with equipment suppliers or referenced sources. Particular care should be taken to distinguish civil costs (plant etc.) from mechanical and engineering costs which will have very different asset lives.

Annualisation of costs can be undertaken through the application of an annualisation factor which depends on the interest rate used and the time horizon. As this factor is not affected by any other conditions time can be saved through the use of look up tables (Annex I).

Costs need to be expressed in constant prices. This means it is necessary to select a base year and convert all costs to this year through the use of price indexes. The actual base year chosen is less relevant than the fact that all costs are expressed in a common year. A variety of price indices are available reflecting different levels of tolerance for uncertainty. The most widely used price index is the retail price index. Much better price indexes, however, are available. Two of the most commonly used price indices are the Construction Output Price Index (COPI) and the Metal Goods Engineering Index (MGEI). The indices for 1980 to 1996 are given in Annex II. COPI should be used for civil construction items and MGEI for mechanical and engineering (M&E) items. A combination of the two indexes may also be used by weighting the indexes according to the proportion of civil and M&E components.

Cost changes and other changes introduced by the option (e.g. output quality) may alter the price, quantity and quality of the output. Therefore, in many cases it will be necessary to examine the operator's forecasts of demand which may include price changes. These need careful consideration for which some suggestions are given below (Section C3.3.2).

Where there is an impact on output or price an allowance may need to be made in the annual cost calculation. This could be done for example by adding the cost of lost sales to the cost of the options. To be consistent with the rest of the methodology, however, this needs to be the direct cost to the company net of any savings.

Supporting information needs to be considered in Stage 5. This may require a consideration of the background economics of the sector (details of which are provided in Section C2), industry sector characteristic (Section C3.3) and sub-sector economic benchmark data (Section C3.5). Other issues such as the profile of costs, timing of investments etc. may also need to be considered.

During this stage and the sensitivity analysis in Stage 6 a broad range of information may need to be considered. The following section provides some guidance on how such information can be given full consideration.

### **C3.2.2 Cost Information**

In preparing and interpreting cost information the following guidance to Operators and Inspectors is given with regard to the sector.

#### **Taking proper account of costs**

The capital and running costs incurred for the application of abatement techniques to an emission problem need to be assessed to select the most economic technique and to judge the cost effectiveness of the technique in terms of the reduction of environmental harm. Although estimation of project capital costs can be an arcane and imprecise craft, Inspectors may wish to enquire more deeply into the makeup of an estimate in order to understand the judgements reached by an operator.

This section explores, briefly, some of the factors that influence an estimate and its preparation.

The most accurate cost evaluations are prepared from detailed schedules of plant items, piping runs, valves, instrument loops, structural steel, cabling, etc. taken from the "approved for construction" drawings. This degree of definition is not usually available at the stage of attempting to select a process. For project estimates without fully detailed design the starting point for cost estimation is the list of the main plant items. The costs of the main plant items might be known from manufacturers' quotations or, for routine items like vessels pumps or heat exchangers, a cost can be extracted from records or a database.

From the costs of the main plant items a crude extrapolation to the fully installed cost can be made by applying multiplying factors of, say, 3 or 5. An illusion of accuracy can be introduced by using subsidiary factors to derive piping, instrumentation, design, civils and so on.

For relatively conventional plants with an extensive list of main plant items, these techniques can be surprisingly accurate. However, the less the number of main plant items required and the more individual the design of the plant installation, the more

likely are the factors to be in error. Nevertheless, a breakdown of an estimate into its components of MPI's, piping, instrumentation, civils construction, electrical and so on will allow the inspector to understand better the features of a particular proposal.

The main components of an estimate are discussed below in order to demonstrate how the estimate is assembled and to indicate some of the distorting features which might occur in applying the methods to emission abatement equipment.

1. Main Plant Items. The cost of main plant items will vary markedly according to the materials of construction and the pressure rating. Actual market prices of MPI's can differ from database values according to the economic cycle. In recession, bargains can be obtained; during booms, premiums may have to be paid. Clearly, these variations in the cost of a major item of equipment should not affect the cost of associated structures, instruments or civil work.
2. Erection Costs. For conventional plants, erection costs can amount to 0.15 of MPI cost. For abatement equipment erected in existing plant, the cost will be related to the complexity of the operation, from a low cost for a simple add-on to a high cost if major modification is required to the existing plant to accommodate the new equipment within its structure.
3. Piping. Piping costs frequently amount to the same value as the MPI cost. Piping will normally be of the same material as the equipment (so the ratio will hold). Variations will occur if larger amounts of piping are required for:
  - the need for many process streams;
  - location of the equipment at a distance from the main plant;
  - complicated hook-up to the supplying plant;
  - large circulating flows needing larger sizes of pipe;
  - Conversely, piping costs: MPI costs can be less for location of equipment close to the main plant;
  - simple hook-up to the applying plant;
  - expensive processing equipment.
4. Instruments. Typically, instrumentation costs 0.3 of MPI costs. This cost is a function of the number of control loops. Costs will increase if complicated on-line analyses are required. The sophistication of the instrumentation will also vary according to the extent to which the instruments are required to ensure the safety of the unit. If transmission links to the control room are required, the costs will increase again.
5. Electrical. Electrical costs are often up to 0.2 of the main plant item cost. For the installation of abatement equipment the factor would normally be expected to be much lower if only a few additional drives are required from an existing system, which can cope with the extra load.
6. Structural. A factor of 0.1 of MPI cost is often used to cover structural costs. The actual structural requirements for abatement equipment might vary from nil for an insertion into an existing structure to major additions if extra height or extra bays are need for the existing structure.

7. **Civil Work.** Civil engineering costs can amount to 0.5 of MPI for conventional plant. Civil costs would be expected to be much less for modification to an existing plant.
8. **Miscellaneous:** This group normally includes items such as lagging, fireproofing, painting. It is likely to represent an insignificant part of plant modification work.

The sum of these eight cost items provides what is known as the Net Cost. The Gross Cost can amount to 1.5 to 2 times the Net Cost.

The difference between the Gross and the Net Costs permits allowances to be made for less tangible items such as supervision, start-up charges, spares, catalysts. Two items, in particular, will be of interest:

- **Design.** The Inspector will wish to be sure that adequate attention has been given to design and hazop considerations. Even when complete packages are bought it is vital that a comprehensive review of the impact on the existing plant has been done. For some modifications an extensive rework of the main plant design will be required;
- **Contingency.** The value inserted for contingency may surprise. Contingencies should not be arbitrary, the contingency factor for a project is derived from consideration of the degree of a number of key elements of the project concept. Painful experience has demonstrated to project managers that the methods of contingency assessment are indeed valid.

### **Factors affecting costs**

Costs will be sensitive to particular factors and proper consideration needs to be given to these factors in assessing NEEC. In the case of VOCs the most important factor affecting costs is likely to be the gas volume flow followed by the inlet concentration. In many cases these will affect the specification of the equipment required for the pollution control and hence costs. Care should be taken to ensure that any "gold-plating" of costs is avoided. The specification of equipment should be the minimum required to achieve the necessary level of abatement or control or any added specification, for example relating to future proofing, should be fully justified.

### **Incremental benefits**

The multi purpose nature of many plants which may be undertaking a number of activities simultaneously may lead to quite complicated linkages between equipment and pollution control activities. Operators should have regard to "creative" solutions on a site specific basis. In some cases there may be incremental benefits from slight alterations in the way the pollution control equipment is applied. In such cases incremental benefits may tip the balance between acceptable and unacceptable levels of cost. Given the complicated nature of many of the sites in question some form of sensitivity analysis may need to be undertaken to cover the range of possibilities that exist.

## Cost allocation

In particular for in house and divisional operations it will need to be demonstrated that the costs (e.g. extra staff costs) are true incremental costs for the option and they would not be otherwise undertaken or economies of scale arise through joint use in other operations. In particular proper consideration and justification of any "on costs" or overheads for staff are needed.

## Financing/sources of funds.

The annualised costs of options will be affected by the way in which the operator seeks to finance the investment and additional operating costs. A consideration of the sources of funds for financing investments needs to be undertaken as this will affect the appropriate cost of capital and hence the annualised costs. Grants, investment offsets against tax, foreign investment funds etc. should also be examined.

To give an idea of the sensitivity of results to the assumption regarding the costs of capital, the following annualised costs result for three schemes which are identical with the exception of the cost of the source of funds.

Cost of capital	8.0%	10.0%	12.0%
Ist year capex	500 000	500 000	500 000
Life time	25	25	25
Annualisation factor	9.4%	11.0%	12.7%
Annualised cost	46 839	55 084	63 750

As can be seen differences of a few percentage points in the assumed cost of capital can lead to large differences in the annualised costs of schemes. The annualisation factors are taken from the look up tables in Annex I.

A variety of sources of funds will be available to the operator. The cost of funds tends to be minimised when the funds are used correctly (i.e. long term finance for long term investment and visa versa).

Different costs of capital may also be appropriate to different options. This is particularly true where there are different levels of capital intensity in the option's operating lives for the equipment involved.

The cost of capital will be associated with the riskiness of the investment. Higher risk will mean a higher cost of borrowed or invested funds. The profile of risk will vary from company to company. Risks and hence costs of capital may be lower where there is a high level of market protection (e.g. through the ownership of patents etc.).

It is not possible to be prescriptive regarding appropriate costs of capital because of the variety of company types being covered - each of which will face a different situation. Costs of capital will be different for debt and equity financing. For debt



financing the cost of risk free debt is generally in the range of 2% to 4%<sup>2</sup>. Any particular company will face a cost of debt capital greater than this depending on its risk profile. The general return to providers of equity finance (investors) is around 7% for the market as a whole (over the long run)<sup>3</sup>. The validity of a company's assumption regarding its own cost of capital can be judged by reference to these baselines and the average returns earned by companies in different sectors (Section C3.5).

Funds to finance environmental investments can be obtained from a variety of sources. These may be internal or external. The cost of internal funds (e.g. retained profit) has a cost associated with the return on the next best alternative use of those funds (opportunity cost). The costs of external funds will generally be clearly defined (e.g. interest on bank loans). Companies will need to justify the cost of capital used on the basis of the source of funds. Alternative sources of funds should also be examined, such as funds for demonstration projects. It should be noted, however, that there has been a general trend away from direct funding contributions towards technology transfer and awareness raising exercises. Where operators are unable to identify their cost of capital the Treasury's recommended rate for commercial sector projects should be used. This rate is currently suggested as a minimum of 8%.

### **Investment Cycles**

High capital equipment costs associated with the level of technology within the sector means that investment cycles will be important in determining the costs of pollution control. An inspector may need to appreciate the point which the company is at with regard to its investment cycle in order to determine the most appropriate option. In some situations delaying pollution control investment so that it avoids expensive retrofitting may be an appropriate solution. This will be particularly true if delaying the investment allows a higher level of pollution control to be achieved. These trade offs can be explored through the use of sensitivity analysis. However, given the long investment cycles of particular firms (e.g. 25 years) and the importance of stepwise growth and growth through acquisition, retrofitting may be inevitable in some situations.

### **C3.2.3 Other Information**

In addition to cost information the operator may supply other information as required. The majority of non-cost information is likely to relate to price/quantity issues. Reductions in output as a result of pollution control expenditure may be added to the costs of pollution control (through an adjustment to the annualised costs) and hence a consideration of prices may be required for the assessment of overall costs.

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<sup>2</sup> In 1996 the generally accepted risk free rate (rate of return on indexed gilts) was 3%

<sup>3</sup> HM Treasury (1997) Appraisal and Evaluation in Central Government

In addition the operator may supply other information about prices/quantity forecasts which will need to be interpreted. It should be noted, that in many situations operators will have made an assessment of future market prospects. For example, in seeking a substantial variation of an authorisation to allow the company to enter a new market it is highly likely that the company will have given consideration to the likely effects of different cost/price/quantity levels on the attractiveness of then investment. This information, if available, will need careful interpretation. Use should be made of the benchmark economic data provided in Section C3.5, in particular in relation to profit margins and returns.

### **Price/quantity forecasts.**

Although not incorporated into the economic assessment methodology operators and inspectors should have regard to the likely market impacts of cost escalation. This may require an assessment of a number of factors:

- because of the variety of products which may be produced and the changing market prospects of these products consideration should be given to the product mix assumptions for any price quantity forecasts. Where possible sensitivities to different assumptions should be made;
- companies will have different exposure to competition from foreign competitors (who may have different environmental cost burdens) in both home and overseas markets. The extent of this competition needs to be established for an assessment of the price/quantity forecasts;
- definition of markets (geographic and commercial) for which products destined;
- information on special customer relationships;
- in examining long term responses to cost increases account needs to be taken of the scope for productivity increases.

### **C3.3 Industry characteristics and implications for the economic assessment**

The following table summarises some of the sector's characteristics and their implications for the NEEC assessment. Annex III is cross-referenced with these factors so that they may be considered at the appropriate point in the economic assessment.

**Table C18 Industry Characteristics and Practical Implications for Economic Assessment of BPEO**

No	Characteristic of sector	Major Implications for Economic Assessment
IS1	Three tiered industry structure: <ul style="list-style-type: none"> <li>• stand alone operators,</li> <li>• divisional operators,</li> <li>• in-house operators.</li> </ul>	<ul style="list-style-type: none"> <li>• Locked in capital for in-house operators. The IPC component of in-house operators may be physically or otherwise locked in to the rest of the plant (upstream or downstream). Changes in the operating conditions for the IPC component of the operation may have spill-over effects into the rest of the operations. Care needs to be taken in specifying the limits of the assessment.</li> <li>• Potential for “creative” cost allocation for in house and divisional companies. Care needs to be taken in interpreting “overhead” or on-costs for the process. For example, on costs may include a contribution to building maintenance - whereas new staff may be accommodated within existing buildings.</li> <li>• Stand alone operators may find it harder to withstand downtime than a larger organisation that can spread costs.</li> </ul>
IS2	Large number of relatively small producers	<ul style="list-style-type: none"> <li>• Exacerbation of impacts on stand alone operators, majority of which are SMEs. Inspectors need to take account of the size of the operation in order to avoid over burdening SMEs. It should not be assumed that the ability of smaller companies to meet pollution abatement requirements relative to larger companies is proportional to their size.</li> <li>• Cost increases may lead to a concentration of industry and a potential loss of market share by SMEs. This may result in loss of market “resilience” - ability to respond to change through diversity.</li> <li>• Smaller operators will generally face higher costs of capital than larger operators.</li> </ul>
IS3	Foreign ownership	<ul style="list-style-type: none"> <li>• There is a large degree of foreign ownership of UK company assets, and of overseas assets by UK companies. This may affect the cost of capital and the attractiveness of investments. Foreign investments can be more susceptible to changes in the return on investment (because the funds are inherently more mobile) which will affect the long term ability of the firms to attract foreign investments.</li> <li>• Care should be taken with firms whose operations are “underpinned” by the investment of a foreign parent organisation. Parent organisations will face a much wider choice of alternative investments and be quicker to liquidate assets in a foreign company.</li> </ul>
IS4	Multi purpose plant with multiple on site activities	<ul style="list-style-type: none"> <li>• May be difficult to adequately separate out the costs for in-house operators or multi purpose plant. Comparison with stand alone operators is recommended.</li> <li>• Often waste streams are combined from different operations prior to final treatment. In such cases wastes from non IPC processes may be combined with wastes from IPC processes and treated together. There is an issue of cost allocation to be considered. In such circumstances costs may need to be allocated. Often a simple shares basis will be sufficient. However, consideration needs to be given to the operator’s treatment of costs in these circumstances. See note on cost allocation under IS1</li> <li>• It should be noted, however, that in general there has been a move away from combining waste streams towards upstream prevention or abatement where the pollutant is more concentrated.</li> </ul>
OPI	Non continuous production/diversity of product range (batch operations)	<ul style="list-style-type: none"> <li>• Vast range of possible products with outputs ranging from a few kilos to 1000 tonnes - may be a need for generic techniques to control a variety of problems in addition to process specific techniques</li> <li>• Process may be used for specific products for variable amounts of time.</li> <li>• Products may have different environmental impacts. Consideration given to likely profile of products over time period with evidence from historical product mixes.</li> </ul>

No	Characteristic of sector	Major Implications for Economic Assessment
OP2	Growth by acquisition	<ul style="list-style-type: none"> <li>• Growth by acquisition is common. Therefore new plant situations are likely to be less frequent than retrofitting or upgrading.</li> <li>• High level of mergers, joint ventures etc. A variety of organisations may be involved in decision making. Inspectors should seek to identify all relevant parties.</li> <li>• Change in ownership may affect level of environmental performance. Environmental performance may be tied to the characteristics and make up of existing management and ownership structures. Changes in ownership should not lead to a down grading of the importance attached to the environment.</li> <li>• Scope for implementing new and improved environmental practices may be greater at the "fluid" stage in management reorganisation. Inspectors should seek to capitalise on the opportunities for change.</li> </ul>
OP3	Factor productivity	<ul style="list-style-type: none"> <li>• Industry shows a track record of productivity improvements. Care should be taken in examining forecasts of costs in the future in particular with regard to forecast market positions. Ignoring scope for productivity improvements will mean a more pessimistic forecast than may be the case</li> </ul>
OP4	Stepwise investment	<ul style="list-style-type: none"> <li>• Large additions to capital in particular periods of firm's growth cycle. New plant construction infrequent - growth by extending existing plant is the norm. Opportunities for large scale changes will be infrequent and the opportunities should be made the most of.</li> <li>• High levels of spare capacity at points in firm's growth cycle. Measures of environmental impact will need to take account of capacity utilisation rather than scale of operations.</li> </ul>
OP5	Capital intensity of production	<ul style="list-style-type: none"> <li>• Capital costs are likely to be more important than operating costs indicating effort should be concentrated on the former.</li> <li>• "Environmental" obsolescence may be very costly for major changes which require new technology rather than upgrading. Consideration should be given to "future proofing" investments to minimise the potential cost implications.</li> </ul>
OP6	Need for flexibility/importance of innovation	<ul style="list-style-type: none"> <li>• Rapid changes in customer requirements due to reliance on market innovation. Need for authorisations which balance the need for flexibility with the need to protect the environment. An emphasis on flexibility within the authorisation, while recognising the environmental impacts, will minimise the potential costs of restrictions.</li> </ul>
OP7	Out-sourcing drive	<ul style="list-style-type: none"> <li>• Out-sourcing may be an option for in house operators faced with increasing environmental costs. Although the UK has moved out of much of the low value end of the product range - some in house producers still rely on in house operations for low value products. Substitution of products with low value foreign alternatives may be the best environmental option in some cases.</li> </ul>
OP8	Variable but low cost raw material	<ul style="list-style-type: none"> <li>• Low incentive for raw material minimisation. Inspectors may need to set authorisations which increase the incentive for minimisation and encourage efficiency. Reference to leading firms should be made.</li> </ul>
OP9	High utility costs	<ul style="list-style-type: none"> <li>• Potential gains from efficiency/recovery techniques may need to be explored.</li> </ul>
PM1	Diversity of product markets - sector and company output find their way into a huge variety of products and applications.	<ul style="list-style-type: none"> <li>• Company growth tends to be tied to general economic activity and therefore cyclical. However given importance of international markets company cycles may not follow UK business cycle. In times of recession home market recession, therefore, business prospects of internationally orientated firms may still be buoyant.</li> <li>• Investment at particular points in the cycle more difficult than otherwise. Industry's ability to afford pollution control expenditure will vary with the investment cycle. Sector has a relatively long investment cycle (about 25 years). Consideration should be given to delaying investment until it can be achieved "organically" (i.e. through natural growth and replacement).</li> </ul>

No	Characteristic of sector	Major Implications for Economic Assessment
		<ul style="list-style-type: none"> <li>Plants built at scale to satisfy general peak demand. Large changes in capacity utilisation and hence possible environmental impact. Capacity utilisation may be an important factor in determining overall costs and alternatives.</li> </ul>
PM2	Mixed product market prospects.	<ul style="list-style-type: none"> <li>Consideration of NEEC is complicated by the diversity of markets into which company is selling.</li> <li>While some sectors of the market are forecast to have strong growth (e.g. pharmaceutical intermediates) others appear to be in steady decline (e.g. agrochemical intermediates).</li> <li>Limited cost pass through for companies in certain sectors.</li> <li>Affordability will be higher in companies operating in growth sectors.</li> </ul>
PM3	Made to order products	<ul style="list-style-type: none"> <li>Limited stock holding. This may reduce the need for storage facilities.</li> </ul>
PM4	Importance of export market and foreign competition.	<ul style="list-style-type: none"> <li>Limited cost pass through particularly where competition is from companies in countries with lower environmental cost burden.</li> <li>Vulnerability to exchange rate fluctuations.</li> </ul>
PM5	Importance of quality/reliability relative to price	<ul style="list-style-type: none"> <li>Impacts on quality and reliability need to be explicitly taken into account in the assessment. The impact of investment on quality and reliability may potentially offset the impact of increased costs</li> </ul>
PM6	Specialisation and niche marketing	<ul style="list-style-type: none"> <li>Domestic competition limited by high levels of niche marketing. Enhanced possibilities for cost pass through because of limited competition in some markets</li> </ul>
PM7	US FDA rules	<ul style="list-style-type: none"> <li>Operators producing pharmaceutical intermediates and food additives subject to US FDA rules on plant operation if selling into the US market. Competitors will face similar constraints.</li> </ul>
PM8	Supplier relationships	<ul style="list-style-type: none"> <li>Special supplier relationships are common, particularly for companies supplying pharmaceutical manufacturers. May be more scope for cost pass through in these situations.</li> </ul>
PM9	EU Pesticides use directive	<ul style="list-style-type: none"> <li>Similar implications for US FDA on agrochemical intermediates.</li> </ul>

### C3.4 Generic pollution cost estimates

Because of the inherent variability of the industry it is not possible to derive cost estimates of various pollution control strategies for the companies. It is felt however, that both operators and inspectors will benefit from some benchmark cost estimates. Cost estimates have therefore been derived for some generic pollution control options. These rely on data developed by ERM and Chem Systems for the analysis of the costs and benefits of the control of VOC emissions. It should be stressed that actual costs are likely to vary considerably due to site to site and company to company variations.

#### C3.4.1 Pollution control options investigated

The following control options were considered:

- *Tank losses.* Control option involves a combination of secondary seals for floating roof tanks and internal floating roofs for fixed roof tanks. The option also involves the use of reflective paint.
- *Loading losses.* Single and secondary stage vapour recovery units
- *Fugitive losses.* Level 1 control (US EPA 453/R-92-018) involving annual inspection of liquid service components and quarterly inspection of gas service components.
- *Tail gases.* Destruction by oxidation for two cases - a concentrated and a dilute stream. Costs include an assumption about piping requirements which can be important.
- *Vents.* Control of flare and occasional vents through extensions to piping, control and flare systems.
- *Losses from water.* Installation of drain seals, air stripping back to process and covering of waste water basis where appropriate.
- *Losses on clean-out.* Improvements to the piping network.

Marginal abatement costs per tonne of VOCs abated are developed for small (50 to 99 employees) and large sized (100-200 employees). The marginal costs of abatement range from £240 per tonne to £25 600 per tonne for large companies and from £0.34 per tonne to £58 400 per tonne for small. The following table summarises marginal abatement costs.

**Table C19 Costs of control options per plant £K**

Control Options	Small firms (50-99 employees)	Large firms (100-200 employees)
Vents: flare	0.3	0.1
Concentrated tail gas	0.7	0.2
Fugitives Level 1	2.9	0.8
Losses on clean-out	2.6	0.8
Dilute tail gas	2.1	1.0
Vents: occasional	4.9	1.4
Tank losses (per tank)	5.9	2.2
Losses from water	8.0	2.4
Loading stage 1 (30 ktpa)	10.0	3.7
Loading stage 2 (30 ktpa)	36.3	12.7
Fugitives Level 2	58.4	25.6

Source: ERM and Chem Systems (1996)

## **C3.5 Sub-sector economic benchmarks**

### **C3.5.1 Introduction**

This section provides benchmark environmental expenditure and economic data for a number of sub-sectors.

#### **SIC Code Designations**

The following SIC codes are provided to link company specific data to the benchmark values provided in this report.

If an SIC code is known it can be related directly to the designation used in this report from below. Where an SIC is not known it can be found through the index in the Standard Industrial Classification of Economic Activities. This uses alphabetical key words to determine the appropriate SIC codes. The key words should relate to the *main* business activity of the company in question.

Where an SIC code is not shown below, the companies were not represented in the sample and no benchmark data will be available. In this case companies could be asked to consider which definition most closely corresponds to them. Benchmark economic data is only provided where consistent sectors have been identified. For example, no benchmark data is available for the "other" category because the companies are too varied to allow benchmarking. In addition for a number of sectors (e.g. Research and Development), lack of information has meant that no benchmarks could be derived.

**Table C20 Benchmark Sectors and SIC designations**

SIC 92 Group	Number	%	SIC 92 Codes
Manufacture of basic pharmaceutical products	23	8%	24.41
Manufacture of food products	6	2%	15.42, 15.89/2
Manufacture of other chemical products nec (in man made fibres)	23	8%	24.62, 24.66, 24.7
Manufacture of other organic basic chemicals	69	25%	24.14
Manufacture of paints, varnishes and similar coatings, printing ink and mastics	9	3%	24.30/1
Manufacture of pesticides and other agro-chemical products	4	1%	24.2
Manufacture of pulp and paper products	4	1%	21.12, 21.212, 21.23
Manufacture of soap and detergents, cleaning and polishing preparations	6	2%	24.51/1, 24.51/2, 24.52
Manufacture of Textiles	8	3%	17.11, 17.3, 17.543, 17.71
Other	19	7%	20.10, 45.31, 50.10, 51.70, 52.48/3, 60.24, 65.12/1, 74.15, 74.84, 90.00
Other manufacturing	29	10%	23.20/1, 23.20/2, 26.12, 26.66, 26.81, 26.82/2, 27.10, 27.42, 27.45, 28.51, 28.75, 29.14, 29.32, 29.53, 31.20, 32.3, 33.10, 33.30/1, 33.40/3, 34.30, 36.63/2
Research and development	6	2%	73.10, 73.0
Manufacture of other plastic and rubber products	31	11%	25.13, 25.24
Wholesale of chemical and other products	40	14%	51.55, 51.62, 51.41, 51.52
Grand Total	277	100%	

### C3.5.2 Sub-sector environmental expenditure data

Information on environmental expenditure of the broad sectors has been extracted from the DoE's report on Environmental Protection Expenditure by Industry. These figures need to be treated with caution as they relate to a single year's information (1996).

**Table C21 Environmental expenditure in related sectors by media**

Sector	Food beverages and tobacco	Textiles and leather products	Pulp and paper products, printing and publishing	Chemicals and man made fibres	Rubber and plastic products
Water	66%	51%	64%	49%	18%
Air	13%	4%	11%	26%	37%
Waste	18%	41%	23%	19%	23%
Noise	2%	3%	0%	0%	1%
Other	0%	0%	1%	6%	22%
Total £m	327	114	368	503	87
Gross output £m	61,150	17,195	33,268	37,022	14,840
% of gross output	0.53%	0.66%	1.10%	1.36%	0.59%



Across all industry the percentage of gross output (i.e. value of sales) accounted for by environmental expenditure is 0.56%. Within the sectors of interest the largest expenditure is by the chemical industry 1.36%. Within most sectors the majority of expenditure is on the water medium - the exception being in the rubber and plastics sector, where expenditure on the air medium is higher.

Environmental protection expenditure includes capital and operating expenditure for that year incurred by companies which can be attributed to an environmental objective. This includes end of pipe investment made to treat or control emissions of waste materials at the end of the production process as well as clean technologies - where the production process is adapted or changed so that it generates fewer emissions or waste materials.

Operating expenditure includes expenditure by companies on their own account (for example for staff working on waste treatment plants) and for payments to others on the purchase of environmental services - e.g. waste management and waste water treatment. The estimates do not include costs to industries from reducing their output for environmental reasons.

The figures are gross figures because they do not involve any allowance for revenue from environmental investments (e.g. by selling spare capacity to other companies).

The following table shows the type of expenditure incurred by companies - distinguishing between capital and operating expenditure, expenditure on end of pipe solutions and on cleaner (integrated) processes. The table also identifies other categories of expenditure such as that on environmentally related R and D.

**Table C22 Environmental protection expenditure by type of expenditure**

Expenditure type	Food beverages and tobacco	Textiles and leather products	Pulp and paper products, printing and publishing	Chemicals and man made fibres	Rubber and plastic products
Capital expenditure on end of pipe control	15%	19%	35%	30%	37%
Capital expenditure on integrated processes	8%	3%	5%	15%	28%
Operating expenditure on end of pipe control	11%	11%	40%	23%	3%
Operating expenditure on integrated processes	0%	1%	0%	3%	2%
External waste and effluent disposal	60%	59%	19%	16%	15%
Research and development	1%	3%	1%	8%	5%
Fines and charges	2%	2%	0%	1%	0%
Green/clean products	3%	3%	1%	4%	9%
Grand total	100%	100%	100%	100%	100%

In the food and textiles related industries the majority of expenditure is on waste and effluent disposal costs paid to third parties - trade effluent charges etc. In other industries capital costs are more important. While operating costs associated with integrated processes are very low they are much higher for end of pipe treatment. Both the chemical and plastics industry spend considerably more resources on environmentally related research and development.

### **C3.5.3 Sub-sector economic data**

This section provides sub-sector economic data to facilitate a comparison of individual companies with sectoral information. The look up SIC information should be used to identify the sub-sectors of interest.

The benchmark summary data relate to size (employee based) current ratios, gearing, return on capital, return on assets, profit margins, net income (profit) efficiencies and asset turnover. For most of the benchmark data averages and confidence limits are provided as low and high cases. The low number of companies (and high variability of reported financial statistics) mean that different levels of confidence are attached to each of the benchmark values. The low and high cases should be interpreted as a range within which 90% of the companies are likely to be found. Companies outside these ranges should be considered as uncharacteristic.

Each sub-sector is dealt with in turn. The following guidance for interpretation is provided to assist Inspectors in drawing conclusions regarding particular companies through benchmark comparisons. In most cases where a company displays an economic variable significantly different from the benchmark average there should be some justification and or explanation.

It should be noted here, however, that poor financial performance should not shield companies from justifiable environmental investments. Instead the benchmarks should be used as a framework within which options and the timing of investments can be discussed.

***Company size:*** Company size is given primarily for comparative purposes. It can be measured in a variety of ways. The number of employees is the measure used here. Aside from background information a consideration of size may help inspectors deal with two important issues:

- economies of scale;
- impact on SMEs.

Economies of scale arise from a variety of conditions (e.g. larger companies will be able to secure purchasing discounts, or operate at lower unit costs because fixed costs are spread over a larger base). The smaller the company the lower the ability to exploit economies of scale.

Smaller firms suffer disadvantages for a number of reasons. Lack of ability to exploit economies of scale is obviously one of these. Others are summarised in Section C2.4.4 and include reactivity, skill shortages, capital constraints and product dependence.

Inspectors may need to make a decision as to whether or not companies suffer from diseconomies of scale or SME disadvantages. The benchmark data table provides information on the relative sizes of companies to assist inspectors in deciding whether or not a company may face such conditions relative to other companies in its sector or related sectors.

The table shows the percentage of firms in various size bands. Those in bands 1 to 3 are technically classified as SMEs. Inspectors should use this information to decide whether or not particular companies are small in relation to the sector size distribution. If firms are small, there will be a greater potential for the company to suffer from SME disadvantages. Larger companies will, conversely have a greater potential to exploit economies of scale and scope.

**Gearing:** As noted in Section C2.7.1 gearing is an important issue for companies and relates to the amount of debt the company is operating with. Gearing shows the proportion of a companies total worth that is owed in debt and for which financing must be paid. Acceptable levels of gearing will vary from company to company.

In general high levels of debt constrain the investment opportunities of companies. The higher the gearing level the more likely the debt will be a burden to the company. High levels of debt may have been accumulated from recent investment - suggesting companies are at the early stages of their investment cycle. High levels of debt may also be indicative of companies being unable to secure non-debt investment funds (equity) because the market views them as a bad prospect.

High levels of debt may be used by companies to suggest that they cannot afford pollution abatement expenditure. Therefore an understanding of the company's long term debt/equity position in relation to the sector average is important. The benchmark data table presents the distribution of companies within each sub-sector according to the gearing. The table also shows average gearing and confidence limits.

In general companies with levels of gearing less than unity will be in a better position than those with gearing rates greater than unity to afford environmental improvements. However, even companies with very high gearing levels may not be in financial difficulty. High levels of gearing, therefore are not a sufficient indicator of inability to afford environmental improvements. The higher the level of gearing the less able, other things being equal, will the company be to secure further funds for environmental improvements. In addition the higher the level of gearing the more risk the company runs of facing a position where, in times of market recession or contraction, financing payments still need to be met.

**Current Ratio:** The current ratio reflects the short term liquidity of firms. It is an important variable as it is a extremely reliable predictor of bankruptcy. Consideration of the benchmark current ratio information will enable Inspectors to understand companies who may regard themselves as being unable to afford pollution abatement expenditure because of short term cash constraints, or because such increased costs would jeopardise the companies operating conditions.

The current ratio measures the size of a companies short term debts relative to its short term assets. A ratio of unity means the company could pay off all of its short term

debts from available, liquid, assets - in the unlikely event that it should be asked to do so. In general CR of greater than 0.7 are considered to be acceptable. The higher the CR above 0.7, the less likely, other things being equal that pollution control investment will lead to short term financial difficulty.

The benchmark data table provide the frequency of companies within different current ratio bands. Average levels and upper and lower bounds are also given. Companies with ratios close to or above the average are unlikely to suffer from short term cash constraints.

**Return on capital employed (ROCE):** The return on capital is a measure of the profitability of enterprises (See Section C2.7.3). Other things being equal the less profitable the company the less able it will be to afford pollution control investment and *visa versa*. An understanding of the range of profitabilities of firms within the sectors of interest will assist Inspectors in making judgements about the firm's ability to afford such investment.

The benchmark data table shows the frequency of firms in various return on capital bands to assist in benchmarking particular companies. The table shows the average return on capital as well as the range within which 90% of firms will be found. Companies with high ROCE in relation to the benchmark companies will be better placed to afford and finance additional pollution control investment.

**Return on Assets (ROA):** Is an alternative measure of profitability to ROCE. The return on assets is generally lower than the return on capital employed because assets are greater than the amount of assets (capital) actually employed. ROA, however, is also an indicator of efficiency. Companies using assets efficiently will in general have a higher return on assets than those operating inefficiently. Companies with a return on assets close to or in excess of the sector average are more likely to be able to afford pollution control investment.

**Profit margin:** Profit margins are an alternative measure of profitability but provide a slightly different insight into the profitability of firms within the sectors of interest. Companies with high profit margins relative to firms operating in the same sector will, other things being equal, be able to absorb cost increases more easily. High profit margins are indicative of strong market placement - perhaps through ownership of patents or some other form of market protection. This ratio is also an indicator of the companies ability to withstand adverse conditions such as falling prices, rising costs or declining sales. Companies with profit margins close to or above the sector average are more likely to be in a position to absorb cost increases.

**Net income efficiency:** Net income efficiency measured in terms of profit per employee can be thought of as a measure of the scope for efficiency improvements. NIEF provides a guide to how effectively the companies labour force is being utilised. Companies operating in the same sector, with higher NIEF will, other things being equal, have the greatest potential to absorb cost increases (assuming the costs can be passed back through increased efficiency) and *visa versa*. Low levels of NIEF are indicative of a degree of slack being built up in the company.

**Asset Turnover:** Asset turnover is a measure of the efficiency with which a company's management generates sales from the assets at its disposal. In conjunction with NIEF this measure provides guidance on how efficiently the company is run. The higher the rate of asset turnover the more efficient the company and, other things being equal, the less scope there may be for further efficiency improvements.

The benchmark tables show frequencies of companies in particular bands. The definition of the bands are shown in the following table.

**Table C23 Key to benchmark data bands**

Class	1	2	3	4	5
Size:	Less than 25	25 to 100	100 to 250	250 to 500	Greater than 500.
Gearing:	Less than 0.5	0.5 to 1	1 to 1.5	1.5 to 2	Greater than 2
Current Ratio:	Less than 0.5	0.5 to 0.7	0.7 to 1	1 to 1.5	Greater than 1.5
ROCE:	Negative	Less than 10%	10% to 20%	20% to 30%	Greater than 30%
ROA:	Negative	Less than 10%	10% to 20%	20% to 30%	Greater than 30%
Profit margin:	Negative	Less than 5%	5% to 10%	10% to 15%	Greater than 15%
Net income efficiency:	Less than £5K	£5K to £10K	£10K to £20K	£20K to £30K	Greater than £30K
Asset Turnover:	Less than 0.75	0.75 to 1	1 to 1.25	1.25 to 1.5	Greater than 1.5

**Table C24 All sectors benchmark summary data**

Benchmark	Scale (% of companies in band)										Average	Low	High
	1	2	3	4	5								
Size (employees) n=212	23	31	26	10	10	220	-	-					
Gearing (ratio) n=158	21	26	27	11	15	1.36	1.16	1.55					
Current ratio (ratio) n=172	5	9	12	36	38	1.68	1.48	1.89					
ROCE (%) n=141	11	32	23	12	21	19	15	22					
ROA (%) n=147	14	54	20	10	2	8	6	9					
Profit margin (%) n=133	13	33	24	18	13	7	6	9					
NIEF (£K) n=108	39	20	20	7	13	16	11	22					
Asset Turnover (ratio) n=135	14	18	19	24	1.37	1.16	1.59						

**Table C25 Manufacture of basic pharmaceutical products benchmark summary data**

Benchmark	Scale (% of companies in band)					Average	Low	High
	1	2	3	4	5			
Size (employees) <i>n=15</i>	33	20	20	20	7	340	-	-
Gearing (ratio) <i>n=18</i>	28	33	22	11	6	0.94	0.74	1.14
Current ratio (ratio) <i>n=19</i>	0	0	16	47	37	1.52	1.27	1.77
ROCE (%) <i>n=17</i>	0	29	29	18	24	23	14	22
ROA (%) <i>n=17</i>	0	53	18	18	12	15	9	21
Profit margin (%) <i>n=17</i>	0	29	24	6	41	17	10	23
NIEF (£K) <i>n=11</i>	27	0	27	18	27	26	11	41
Asset Turnover (ratio) <i>n=17</i>	24	29	24	18	6	1.02	0.89	1.16

**Table C26 Manufacture of food products benchmark summary data**

Benchmark	Scale (% of companies in band)						Average	Low	High
	1	2	3	4	5	6			
Size (employees) n=6	0	33	33	0	0	0	160	-	-
Gearing (ratio) n=2	0	0	50	50	0	0	1.41	1.20	1.62
Current ratio (ratio) n=2	50	0	50	0	0	0	0.84	0.60	1.09
ROCE (%) n=2	0	0	0	0	100	0	40	35	45
ROA (%) n=2	0	0	50	50	0	0	17	13	21
Profit margin (%) n=2	0	0	0	100	0	0	13	11	14
NIEF (£K) n=2	0	0	50	0	50	0	4	54	2
Asset Turnover (ratio) n=2	0	0	50	50	0	0	1.32	1.21	1.43



**Table C27**    **Manufacture of other chemical products benchmark summary data**

Benchmark	Scale (% of companies in band)						Average	Low	High
	1	2	3	4	5	6			
Size (employees) <i>n=14</i>	21	36	36	0	7		160	-	
Gearing (ratio) <i>n=17</i>	24	41	12	12	12		1.39	0.74	2.04
Current ratio (ratio) <i>n=18</i>	6	6	33	50	6		1.72	1.30	2.14
ROCE (%) <i>n=15</i>	7	33	40	13	7		12	8	17
ROA (%) <i>n=15</i>	7	73	20	0	0		6	3	8
Profit margin (%) <i>n=13</i>	7	36	29	29	0		7	5	9
NIBF (£K) <i>n=9</i>	44	22	33	0	0		7	4	10
Asset Turnover (ratio) <i>n=14</i>	14	36	21	21	7		1.06	0.85	1.27

**Table C28 Manufacture of other organic basic chemicals benchmark summary data**

Benchmark	Scale (% of companies in band)										Average	Low	High
	1	2	3	4	5								
Size (employees) n=50	30	30	28	6	6	160	-	-	-	-			
Gearing (ratio) n=39	15	21	31	13	21	1.67	1.22	2.12					
Current ratio (ratio) n=39	13	13	23	46	5	1.48	1.28	1.68					
ROCE (%) n=30	3	42	3	23	29	19	15	24					
ROA (%) n=31	3	52	32	13	0	9	7	12					
Profit margin (%) n=30	3	43	17	20	17	7	5	9					
NIEF (£K) n=22	32	23	23	14	9	21	4	40					
Asset Turnover (ratio) n=30	17	13	20	27	23	1.26	1.08	1.44					

**Table C29 Manufacture of paints, varnishes and similar coatings benchmark summary data**

	Scale (% of companies in band)							
Benchmark	1	2	3	4	5	Average	Low	High
Size (employees) <i>n=24</i>	11	33	33	22	0	200		
Gearing (ratio) <i>n=6</i>	17	0	50	0	33	1.65	0.83	2.46
Current ratio (ratio) <i>n=6</i>	17	17	50	17	0	2.57	0.32	4.82
ROCE (%) <i>n=6</i>	17	33	0	33	17	14	5	23
ROA (%) <i>n=6</i>	12	50	33	0	0	5	1	8
Profit margin (%) <i>n=6</i>	17	33	50	0	0	3	1	6
NIBF (£K) <i>n=6</i>	50	50	0	0	0	4	1	8
Asset Turnover (ratio) <i>n=6</i>	0	17	17	50	17	1.35	1.08	1.41

**Table C30 Manufacture of pesticides and other agro-chemical products benchmark summary data**

Benchmark	Scale (% of companies in band)					Average	Low	High
	1	2	3	4	5			
Size (employees) <i>n=9</i>	0	0	75	25	0	170	-	-
Gearing (ratio) <i>n=3</i>	33	33	0	33	0	1.01	0.44	1.59
Current ratio (ratio) <i>n=3</i>	0	0	67	33	0	1.35	1.05	1.66
ROCE (%) <i>n=3</i>	0	0	100	0	0	12	11	13
ROA (%) <i>n=3</i>	0	100	0	0	0	7	5	9
Profit margin (%) <i>n=3</i>	0	33	33	33	0	7	5	10
NIEF (£K) <i>n=3</i>	0	67	0	0	33	16	2	30
Asset Turnover (ratio) <i>n=3</i>	0	33	67	0	0	1.03	0.88	1.18

**Table C31 Manufacture of pulp and paper products benchmark summary data**

	Scale (% of companies in band)							
<b>Benchmark</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>Average</b>	<b>Low</b>	<b>High</b>
Size (employees) <i>n=1</i>	25	25	0	50	0	190	-	-
Gearing (ratio) <i>n=4</i>	0	50	25	0	25	1.29	0.64	1.93
Current ratio (ratio) <i>n=4</i>	0	0	75	25	0	1.36	1.21	1.51
ROCE (%) <i>n=2</i>	0	0	100	0	0	16	15	17
ROA (%) <i>n=2</i>	0	0	100	0	0	11	11	11
Profit margin (%) <i>n=2</i>	0	0	0	100	0	11	10	11
NIEF (£K) <i>n=3</i>	0	50	0	50	0	16	1	32
Asset Turnover (ratio) <i>n=2</i>	0	50	50	0	0	1.02	0.97	1.07

**Table C32 Manufacture of soap and detergents, cleaning and polishing preparations benchmark summary data**

Benchmark	Scale (% of companies in band)					Average	Low	High
	1	2	3	4	5			
Size (employees) <i>n=4</i>	67	0	17	0	17	190	-	-
Gearing (ratio) <i>n=4</i>	0	0	50	50	0	1.52	1.34	1.70
Current ratio (ratio) <i>n=4</i>	0	0	75	25	0	1.44	1.24	1.65
ROCE (%) <i>n=2</i>	0	50	50	0	0	9	8	11
ROA (%) <i>n=2</i>	0	100	0	0	0	5	3	8
Profit margin (%) <i>n=2</i>	0	100	0	0	0	3	1	5
NIEF (£K) <i>n=2</i>	50	50	0	0	0	5	-2	12
Asset Turnover (ratio) <i>n=2</i>	0	0	0	0	100	1.93	1.44	2.42

**Table C33 Manufacture of Textiles benchmark summary data**

Benchmark	Scale (% of companies in band)							Average	Low	High
	1	2	3	4	5					
Size (employees) n=6	33	0	50	17	0		200			
Gearing (ratio) n=7	43	0	29	14	14		1.06	0.47	1.64	
Current ratio (ratio) n=8	38	0	13	50	0		1.83	1.11	2.55	
ROCE (%) n=8	38	25	13	0	25		28	2	55	
ROA (%) n=8	38	50	0	13	0		5	0	11	
Profit margin (%) n=7	43	29	0	14	14		4	-1	9	
NIEF (£K) n=6	67	17	0	0	17		17	-9	43	
Asset Turnover (ratio) n=7	29	14	0	14	43		1.12	0.82	1.42	

**Table C34 Manufacture of other plastic and rubber products benchmark summary data**

Benchmark	Scale (% of companies in band)						Average	Low	High
	1	2	3	4	5	6			
Size (employees) n=24	8	42	17	25	8	570	-	-	
Gearing (ratio) n=27	26	22	37	4	11	1.33	0.79	1.86	
Current ratio (ratio) n=29	3	14	38	41	3	1.78	1.35	2.22	
ROCE (%) n=27	19	26	22	7	26	19	8	29	
ROA (%) n=28	21	50	11	14	4	7	2	12	
Profit margin (%) n=25	24	16	44	8	8	6	3	9	
NIEF (£K) n=22	36	9	27	4	23	26	12	40	
Asset Turnover (ratio) n=25	8	12	12	32	36	2.10	1.02	3.17	



**Table C35 Wholesale of chemical and other products benchmark summary data**

Benchmark	Scale (% of companies in band)					Average	Low	High
	1	2	3	4	5			
Size (employees) <i>n=32</i>	25	25	25	0	25	140	-	-
Gearing (ratio) <i>n=4</i>	50	25	0	0	25	1.14	0.12	2.16
Current ratio (ratio) <i>n=6</i>	0	17	50	33	0	3.60	0.22	6.99
ROCE (%) <i>n=2</i>	33	0	33	33	0	9	-4	23
ROA (%) <i>n=3</i>	33	0	33	33	0	10	0	20
Profit margin (%) <i>n=3</i>	33	0	0	33	33	8	2	15
NIEF (£K) <i>n=1</i>	0	0	0	100	0	21	-	-
Asset Turnover (ratio) <i>n=3</i>	0	33	0	0	67	1.49	1.06	1.13

## **C3.6 Other sources of information**

A number of potential sources of information are available to the inspectors and indeed operators. A number of these sources are summarised below.

### **C3.6.1 Published sources**

Department of Trade and Industry (1994) A study of the UK's competitive position in the specialised organic chemicals sector. Provides:

- background information on the sector and addresses for further information;
- sector definition issues, world market etc.;
- company profiles are provided on a number of firms.

This report, however, is four years out of date but remains an important source of background information.

### **Office for National Statistics - Sector Review: Chemicals, Rubber and Plastic Products (Quarterly)**

Contains broad sector information on trends in the industry as well as detailed breakdowns of individual sectors and a macroeconomic summary. Areas covered include: production and productivity, imports and exports, stocks, sales and prices, employment, wages, number of enterprises, employment by region, market analysis, outward and inward investment, research and development expenditure. Areas covered soaps and detergents, perfumes and toilet preparations, essential oils etc. More detailed information can be sourced in the Business Monitor series (full references are given in the Sector Review)

### **Dunn and Bradstreet**

Dunn and Bradstreet can supply a variety of information on particular companies, including: indicator of import and export status, current assets and liabilities, debtors (short term assets), gearing, profits, sales, etc.

### **Barclays Bank Economic Department Industry Update Chemicals (Quarterly)**

Provides a regular update of economic conditions in the industry.

### **C3.6.2 On line sources**

- ABI/INFORM - Business Journal Abstracts
- Knight Ridder - databases covering the chemicals and pharmaceuticals sectors (technical, financial and environmental) including market research reports.

### **C3.7 Summary**

This section provides information to assist Inspectors in undertaking the process specific economic assessment. The variability of companies operating within this sector precludes any hard and fast rules. However, this section has attempted to highlight the main issues which are likely to be encountered in undertaking an economic assessment.

The main elements of the NEEC approach outlined in this sector are:

- A recommendation and qualifications to the use of the BPEO assessment guidelines.
- An illustration of industry sector characteristics and their potential implications for the NEEC assessment.
- Information on benchmark economic and financial data which will assist Inspectors in considering company specific information.



## ANNEX I - EQUIVALENT ANNUAL VALUE FACTORS

Discount Rate or Cost of Capital %								
Years	5	6	7	8	9	10	11	12
5	0.231	0.237	0.244	0.250	0.257	0.264	0.271	0.277
10	0.130	0.136	0.142	0.149	0.156	0.163	0.170	0.177
15	0.096	0.103	0.110	0.117	0.124	0.131	0.139	0.147
20	0.080	0.087	0.094	0.102	0.110	0.117	0.126	0.134
25	0.071	0.078	0.086	0.094	0.102	0.110	0.119	0.127
30	0.065	0.073	0.081	0.089	0.097	0.106	0.115	0.124
35	0.061	0.069	0.077	0.086	0.095	0.104	0.113	0.122
40	0.058	0.066	0.075	0.084	0.093	0.102	0.112	0.121
45	0.056	0.065	0.073	0.083	0.092	0.101	0.111	0.121
50	0.055	0.063	0.072	0.082	0.091	0.101	0.111	0.120
55	0.054	0.063	0.072	0.081	0.091	0.101	0.110	0.120
60	0.053	0.062	0.071	0.081	0.091	0.100	0.110	0.120
Discount Rate or Cost of Capital %								
Years	13	14	15	16	17	18	19	20
5	0.284	0.291	0.298	0.305	0.313	0.320	0.327	0.334
10	0.184	0.192	0.199	0.207	0.215	0.223	0.230	0.239
15	0.155	0.163	0.171	0.179	0.188	0.196	0.205	0.214
20	0.142	0.151	0.160	0.169	0.178	0.187	0.196	0.205
25	0.136	0.145	0.155	0.164	0.173	0.183	0.192	0.202
30	0.133	0.143	0.152	0.162	0.172	0.181	0.191	0.201
35	0.132	0.141	0.151	0.161	0.171	0.181	0.190	0.200
40	0.131	0.141	0.151	0.160	0.170	0.180	0.190	0.200
45	0.131	0.140	0.150	0.160	0.170	0.180	0.190	0.200
50	0.130	0.140	0.150	0.160	0.170	0.180	0.190	0.200
55	0.130	0.140	0.150	0.160	0.170	0.180	0.190	0.200
60	0.130	0.140	0.150	0.160	0.170	0.180	0.190	0.200



## ANNEX II - PRICE INDICES

Year	Construction Output Price Index (COPD)	Metal Goods Engineering Index (MGEI)
1980	100	100
1981	105	107
1982	103	114
1983	105	119
1984	107	126
1985	112	134
1986	118	140
1987	125	146
1988	140	152
1989	158	160
1990	164	170
1991	156	180
1992	145	185
1993	139	190
1994	144	194
1995	158	201
1996	165	205





## **ANNEX III - ECONOMIC ASSESSMENT PROCEDURE**

This annex provides guidance to inspectors and operators on the procedure for undertaking the economic assessment to assist them in considering the issues raised by the application of NEEC to the Speciality Organic Chemicals sector.

## Stages in the economic assessment methodology

