Sector Guidance Note IPPC S4.03

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Guidance for the Inorganic Chemicals Sector

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Table 0.1: Record of changes

Version	Date	Change	Template Version
Draft 1	12 May 2004		v6.2 -12 May 2004
Draft 1.1 (Consultation)	10 June 2004	Section 2.1.1 moved to 3.3, plus errors corrected	v6.2 -12 May 2004

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Executive summary

Status of this Guidance

This guidance has been produced by the Environment Agency, along with the Scottish Environment Protection Agency (SEPA) and the Northern Ireland Environment and Heritage Service (EHS) - each referred to as “the Regulator” throughout this document. Its publication follows consultation with industry, government departments and non-governmental organisations.

What is IPPC

Integrated Pollution Prevention and Control (IPPC) is a regulatory system that employs an integrated approach to control all environmental impacts of certain listed industrial activities. In the UK, the IPPC Directive is implemented through the English and Welsh, the Scottish, and the Northern Irish versions of the Pollution Prevention and Control (PPC) Regulations. It involves determination by the Regulator of the appropriate controls for those industries to protect all environmental media, through a single permitting process. To gain a PPC Permit, an Operator has to demonstrate in its Application, in a systematic way, that the techniques it is using or is proposing to use, both represent the use of Best Available Techniques (BAT), taking account of relevant local factors, and meet other relevant statutory requirements.

This Guidance and the BREF

Much UK Technical Guidance on what is BAT is based on the “BAT Reference documents” (“BREFs”) produced by the European Commission. BREFs are the result of exchanges of information between member states and industry, with most covering individual industrial sectors, and some (“horizontal” BREFs) covering cross-sectoral subjects. UK Technical Guidance Notes are designed to complement BREFs, and take into account information contained in relevant BREFs in setting out indicative BAT standards and expectations for England and Wales, Scotland and Northern Ireland.

The aims of this Guidance

The aim of the Guidance is to provide Operators and officers of the Regulator with advice on indicative standards of operation and environmental performance, relevant to the industrial sector concerned. It also aims (through linkage with the Permit Application Form template) to provide a clear structure and methodology for Operators to follow to demonstrate they have addressed adequately all aspects of the PPC Regulations and relevant aspects of other environmental Regulations. Also, by expressing BAT techniques as clear indicative standards wherever possible, it aims to minimise the effort involved for both Operator and Regulator in the permitting of an installation.

To further assist Operators and officers, separate horizontal guidance is available on a range of topics such as noise, odour, waste minimisation, monitoring, calculating stack heights and so on. Most of this guidance is available free through the Environment Agency, SEPA or EHS (Northern Ireland) websites (see **References**).

Key environmental issues

The key environmental issues for this sector are:

- **Fugitive emissions to air -** Many inorganics installations handle solid materials, which can be the source of fugitive releases of dust and small particulates. In other processes there is the potential for escapes of acid gases, ammonia, VOCs and volatile inorganic compounds.
- **Point source emissions to air -** Most installations have abatement systems for particulates, acid gases, ammonia or volatile organics or inorganics, but there is scope for improvement in emissions from a large number of them.
- **Waste minimisation and waste disposal routes -** The Landfill Directive has reduced the options for disposal of many chemical waste streams so opportunities to minimise waste production and move up the waste hierarchy must be taken.
- **Emissions to water -** A number of installations have effluent streams containing pollutants like heavy metal compounds or complexes which need to be treated separately before being discharged to communal treatment facilities.

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1 Introduction

The status and aims of this Guidance

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

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

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

1.1 Understanding IPPC

IPPC and the Regulations

Integrated Pollution Prevention and Control (IPPC) is a regulatory system that employs an integrated approach to control the environmental impacts of certain listed industrial activities. It involves determination by the Regulator of the appropriate controls for those industries to protect the environment, through a single permitting process. To gain a Permit, Operators have to demonstrate in their Applications, in a systematic way, that the techniques they are using or are proposing to use, are the Best Available Techniques (BAT) for their installation, and meet certain other requirements, taking account of relevant local factors.

The essence of BAT is that the techniques selected to protect the environment should achieve an appropriate balance between environmental benefits and the costs incurred by Operators. However, whatever the costs involved, no installation may be permitted where its operation would cause significant pollution.

IPPC operates under **The Pollution Prevention and Control Regulations** (for equivalent legislation in Scotland and N Ireland see **Appendix 2**). The three regional versions of the PPC Regulations implement in the UK the EC Directive on IPPC (96/61/EC). Further information on the application of IPPC/PPC, together with Government policy and advice on the interpretation of the English & Welsh Regulations, can be found in **IPPC: A Practical Guide** published by the Department for Environment, Food and Rural Affairs (Defra). Equivalent guidance on the Scottish Regulations is provided in PPC Regulations: A Practical Guide (Part A Activities), published by the Scottish Executive and SEPA. The Department of the Environment, Northern Ireland has published equivalent guidance on its Regulations.

Installation based, NOT national emission limits

The BAT approach of IPPC differs from regulatory approaches based on fixed national emission limits (except where General Binding Rules or Standard Permits are issued). The legal instrument that ultimately defines BAT is the Permit, and Permits can only be issued at the installation level.

Indicative BAT Standards

Indicative BAT standards are laid out in national guidance (such as this) and, where relevant, should be applied unless a different standard can be justified for a particular installation. BAT includes the technical components, process control, and management of the installation given in Section 2, and the benchmark levels for emissions identified in Section 3. Departures from those benchmark levels can be justified at the installation level by taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. If any mandatory EU emission limits or conditions are applicable, they must be met, but BAT may go further (see “BAT and EQS” below).

Some industrial sectors for which national guidance is issued are narrow and tightly defined, whilst other sectors are wide and diffuse. This means that where the guidance covers a wide variety of processes, and individual techniques are not described in detail, the techniques (and their associated emission levels) which might constitute BAT for a particular operation, are more likely to differ, with justification, from the indicative BAT standards than would be the case for a narrow, tightly-defined sector.

BAT and EQS

The BAT approach complements, but differs fundamentally from, regulatory approaches based on Environmental Quality Standards (EQS). Essentially, BAT requires measures to be taken to prevent emissions - and measures that simply reduce emissions are acceptable only where prevention is not practicable. Thus, if it is economically and technically viable to reduce emissions further, or prevent them altogether, then this should be done irrespective of whether or not EQSs are already being met. The BAT approach requires us not to consider the environment as a recipient of pollutants and waste, which can be filled up to a given level, but to do all that is practicable to minimise emissions from industrial activities and their impact. The BAT approach first considers what emission prevention can reasonably be achieved (covered by Sections 2 and 3 of this Guidance) and then checks to ensure that the local environmental conditions are secure (see **Section 4** of this Guidance and also Guidance Note**Environmental Assessment and Appraisal of BAT**). The BAT approach is therefore the more precautionary one because the release level achieved may be better than that simply required to meet an EQS.

Conversely, if the application of indicative BAT might lead to a situation in which an EQS is still threatened, a more effective technique is required to be BAT for that installation. The Regulations allow for expenditure beyond indicative BAT where necessary, and, ultimately, an installation will only be permitted to operate if it does not cause significant pollution.

Further advice on the relationship between BAT, EQSs and other related standards and obligations is given in **IPPC: A Practical Guide**, its Scottish equivalent, and also in Section 3.

Assessing BAT at the sector level

The assessment of indicative BAT takes place at a number of levels. At the European level, the European Commission issues a “BAT reference document” (BREF) for each main IPPC sector. It also issues “horizontal” BREFs for a number of general techniques which are relevant across a series of industrial sectors. The BREFs are the result of an exchange of information between regulators, industry and other interested parties in Member States. Member States should take them into account when determining BAT, but they are allowed flexibility in their application. UK Sector Guidance Notes like this one take account of information contained in relevant BREFs and set out current indicative standards and expectations in the UK. At national level, techniques that are considered to be BAT should represent an appropriate balance of costs and benefits for a typical, well-performing installation in the sector concerned. They should also be affordable without making the sector as a whole uncompetitive, either within Europe or world-wide.

The BREF production programme is in progress, but is not yet complete. The BREF for the Chlor-alkali sector was published in 2000 but the 3 other BREFs for the Inorganics sector are not expected to be published before end-2004 (Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilizers) or mid-2005 (Large Volume Inorganic Chemicals - Solids and Others, and Speciality Inorganic Chemicals). The “horizontal” BREF for the Treatment of Waste Water and Waste Gas has been published, and the BREF for the Storage of Chemicals should be completed in late-2004. The indicative standards laid down in this Note are therefore based on Best Available Techniques Not Entailing Excessive Cost (“BATNEEC”) standards from the two IPC Technical Guidance Notes for Acids and Halogens, and Inorganic Chemicals, together with information from available BREFs (**Ref 1**), where relevant. When all the BREFs for this sector are published, this Guidance Note will be revised.

Assessing BAT at the installation level

When assessing applicability of sectoral indicative BAT standards at the installation level, departures may be justified in either direction. Selection of the technique which is most appropriate may depend on local factors and, where the answer is not self-evident, an installation-specific assessment of the costs and benefits of the available options will be needed. The Regulator’s guidance **Environmental Assessment and Appraisal of BAT** and its associated software tool may help with the assessment. Individual installation or company profitability (as opposed to profitability of the relevant sector as a whole) is not a factor to be considered, however.

In the assessment of BAT at the installation level, the cost of improvements and the timing or phasing of that expenditure, are always factors to be taken into account. However, they should only be major or decisive factors in decisions about adopting indicative BAT where:

- the installation’s technical characteristics or local environmental conditions can be shown to be so different from those assumed in the sectoral assessment of BAT described in this guidance, that the indicative BAT standards may not be appropriate; or
- the BAT cost/benefit balance of an improvement only becomes favourable when the relevant item of plant is due for renewal/renovation (eg. change to a different design of furnace when the existing furnace is due for a rebuild). In effect, these are cases where BAT for the sector can be expressed in terms of local investment cycles; or

- a number of expensive improvements are needed. In these cases, a phasing programme may be appropriate - as long as it is not so drawn out that it appears to be rewarding a poorly performing installation.

In summary, departures by an individual installation from indicative BAT for its sector may be justified on the grounds of the technical characteristics of the installation concerned, its geographical location and the local environmental conditions - but not on the basis of individual company profitability, or if significant pollution would result. Further information on this can be found in **IPPC: A Practical Guide** and **IPPC Part A(1) Installations: Guide for Applicants**, or the equivalent Scottish Guidance.

Innovation

The Regulators encourage the development and introduction of innovative techniques that advance indicative BAT standards criteria, ie. techniques which have been developed on a scale which reasonably allows implementation in the relevant sector, which are technically and economically viable and which further reduce emissions and their impact on the environment as a whole. One of the main aims of the PPC legislation is continuous improvement in the overall environmental performance of installations as a part of progressive sustainable development. This Sector Guidance Note describes the indicative BAT standards at the time of writing but Operators should keep up-to-date with improvements in technology - and this Guidance note cannot be cited as a reason for not introducing better available techniques. The technical characteristics of a particular installation may also provide opportunities not foreseen in the Guidance, and as BAT is determined at the installation level (except in the case of General Binding Rules (GBRs)), it is a requirement to consider these even where they go beyond the indicative Standards.

New installations

Indicative BAT standards apply, where relevant, to both new and existing installations, but it will be more difficult to justify departures in the case of new installations (or new activities in existing installations) - and for new activities, techniques which meet or exceed indicative BAT requirements should normally be in place before operations start.

Existing installations - standards

For an existing installation, it may not be reasonable to expect compliance with indicative BAT standards immediately if the cost of doing so is disproportionate to the environmental benefit to be achieved. In such circumstances, operating techniques that are not at the relevant indicative BAT standard may be acceptable, provided that they represent what is considered BAT for that installation and otherwise comply with the requirements of the Regulations. The determination of BAT for the installation will involve assessment of the technical characteristics of the installation and local environmental considerations, but where there is a significant difference between relevant indicative BAT and BAT for an installation, the Permit may require further improvements on a reasonably short timescale.

Existing installations - upgrading timescales

Where there are departures from relevant indicative BAT standards, Operators of existing installations will be expected to have upgrading plans and timetables. Formal timescales for upgrading will be set as Improvement Conditions in the Permits. See **Section 1.4.2** for more details.

1.2 Making an application

For the issue of a Permit a PPC Application has to:

- address the issues in Sections 2 and 3 of this guidance;
- assess the environmental impact described in Section 4 (and for England and Wales also in **Environmental Assessment and Appraisal of BAT (IPPC H1)**);
- demonstrate that the proposed techniques are BAT for the installation.

In practice, many PPC Applications have contained far more information than is needed for determination, yet have not addressed the areas that are most important - and this has led to extensive requests for further information. In an attempt to focus application responses to the areas of concern to the Regulator, Application forms (templates) have been produced by the Environment Agency, by SEPA and by EHS in N Ireland. In addition, as the dates for application have approached, the operators in most industrial sectors in England and Wales have been provided with Compact Discs (CDs) which contain all relevant Application Forms and Assessment tools, technical and administrative guidance, BREFs, and the charging scheme (known as EPOPRA), hyper-linked together for ease of use.

There is such a CD for the Inorganic Chemicals sector in England and Wales. The tools and advice on the CD should steer the operator through the PPC application process, define more closely the level of detail required in the Application and help to make the process of calculating impact assessments much simpler.

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

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

1.3 Installations covered

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

Installations for the manufacture or use of inorganic chemicals are listed for regulation in Section 4.2 of Schedule 1 to the Regulations, and the manufacture of chemical fertilizers is listed in Section 4.3. A few inorganic installations may also be described in Section 4.7 - "Manufacturing activities involving carbon disulphide or ammonia".

Part A(1)

Section 4.2 - Inorganic Chemicals

(a) Producing inorganic chemicals such as:

(i) gases, such as ammonia, hydrogen chloride, hydrogen fluoride, hydrogen cyanide, hydrogen sulphide, oxides of carbon, sulphur compounds, oxides of nitrogen, hydrogen, oxides of sulphur, phosgene;

(ii) acids, such as chromic acid, hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, phosphoric acid, nitric acid, sulphuric acid, oleum and chlorosulphonic acid;

(iii) bases, such as ammonium hydroxide, potassium hydroxide, sodium hydroxide;

(iv) salts, such as ammonium chloride, potassium chlorate, potassium carbonate, sodium carbonate, perborate, silver nitrate, cupric acetate, ammonium phosphomolybdate;

(v) non-metals, metal oxides, metal carbonyls or other inorganic compounds such as calcium carbide, silicon, silicon carbide, titanium dioxide;

(vi) halogens or interhalogen compound comprising two or more of halogens, or any compound comprising one or more of those halogens and oxygen.

(b) Unless falling within another Section of this Schedule, any manufacturing activity which uses, or which is likely to result in the release into the air or into water of, any halogens, hydrogen halides or any of the compounds mentioned in paragraph (a)(vi), other than the treatment of water by chlorine.

(c) Unless falling within another Section of this Schedule, any manufacturing activity involving the use of hydrogen cyanide or hydrogen sulphide.

(d) Unless falling within another Section of this Schedule, any manufacturing activity, other than the application of a glaze or vitreous enamel, involving the use of any of the following elements or compound of those elements or the recovery of any compound of the following elements - antimony, arsenic, beryllium, gallium, indium, lead, palladium, platinum, selenium, tellurium, thallium - where the activity may result in the release into the air of any of those elements or compounds or the release into water of any substance listed in paragraph 13 of Part 2 of this Schedule.

(e) Recovering any compound of cadmium or mercury.

(f) Unless falling within another Section of this Schedule, any manufacturing activity involving the use of mercury or cadmium or any compound of either element or which may result in the release into air of either of those elements or their compounds.

(g) Unless carried out as part of any other activity falling within this Schedule -

(i) recovering, concentrating or distilling sulphuric acid or oleum;

(ii) recovering nitric acid;

(iii) purifying phosphoric acid.

(h) Any manufacturing activity (other than the manufacture of chemicals or glass or the coating, plating or surface treatment of metal) which -

(i) involves the use of hydrogen fluoride, hydrogen chloride, hydrogen bromide or hydrogen iodide or any of their acids; and

(ii) may result in the release of any of those compounds into the air.

(i) Unless carried out as part of any other activity falling within this Schedule, recovering ammonia.

(j) Extracting any magnesium compound from sea water.

Section 4.3- Chemical Fertilizer Production

(a) Producing (including blending which is related to their production), phosphorus, nitrogen or potassium based fertilizers (simple or compound fertilizers).

(b) Converting chemical fertilizers into granules.

Section 4.7 - Manufacturing activities involving Carbon disulphide or Ammonia

(a) Any manufacturing activity which may result in the release of carbon disulphide into the air.

(b) Any activity for the manufacture of a chemical which involves the use of ammonia or may result in the release of ammonia into the air other than an activity in which ammonia is only used as a refrigerant.

The installation will also include **associated activities** which have a technical connection with the main activities and which may have an effect on emissions and pollution, as well as the main activities described above. These may involve activities such as:

- the storage and handling of raw materials;
- the storage and despatch of finished products, waste and other materials;
- the control and abatement systems for emissions to all media;
- waste treatment or recycling.

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

This Note contains some information from the Chlor-alkali sector BREF and also from other relevant BREFs or draft BREFs (**Ref 1**) but it leans most heavily on the IPC Technical Guidance Notes for Inorganic Chemicals and Inorganic Acids and Halogens (**Ref 21**).

1.4 Timescales

1.4.1 Permit review periods

Permits are likely to be reviewed as follows:

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

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

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

1.4.2 Upgrading timescales for existing plant

Existing installation timescales

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

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

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

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

1.5 Key issues

The Inorganic Chemicals sector comprises a large number of specifically different installations with relatively few common factors. With the majority of activities undertaken by only one or two operators and only a handful undertaken by more than 3 operators, the main environmental issues tend to be site-specific. However a few general issues are:

1.5.1 Fugitive emissions to air

Many inorganic processes involve the handling of solid materials and fugitive releases of dust and small particulates from joints in conveyors systems, from stock-piles, from packages, etc. are significant issues on many plants. In other processes, where gases or liquids with moderately high vapour pressures are handled, there is always the potential for releases of acid gases, ammonia, VOCs or volatile inorganic compounds from flanges, pumps, agitators and valves with seals, storage tanks, tanker connections, sample points, etc.

These fugitive releases can occur through relaxation or progressive wear-and-tear of sealing materials, through sloppy operation, maintenance or design, or through failure of equipment. Apart from releases of material through accidental mal-operation or equipment failure, fugitive losses from individual pieces of equipment are often small - but on a large-scale plant the aggregated effect can be very significant.

Section 2.2.4 - Control of fugitive emissions to air - of this Guidance Note covers relevant issues and, in addition, prevention and control of fugitive emissions is covered in the Emissions from Storage BREF and in other relevant BREFs. (**Ref 1**)

The basic rules are:

- Operators should aim to minimise fugitive releases of solids, liquid and gaseous substances at the design stage by the specification of the right equipment and the right materials of construction. The priority is environmental protection rather than financial savings from material that is not lost.
- For on-going fugitive emission prevention, operators should have formal inspection/detection programmes in place and, where necessary, replace equipment which continues to generate significant fugitive emissions, with higher quality items.

1.5.2 Point source emissions to air

As with fugitive emissions, many inorganic processes involving the handling of solid materials release significant quantities of dust, fume or wet particulates from process vents - and some of these contain toxic substances such as heavy metal compounds. Other installations release significant quantities of acid gases, ammonia or volatile inorganic or organic compounds from process vents on vessels, storages and abatement system exhausts. On most plants, gaseous emissions from point sources have been individually characterised and significantly reduced (in total) since the introduction of the IPC regime across the sector in the mid-1990s. However, areas remain where considerable improvement can still be made - and for some installations IPC Improvement Programme conditions are still in the process of being completed.

Individual sources of air emissions from particular processes are indicated in **Section 2.1** - In-process controls - in this Note, and further details are provided in the relevant BREF, where available. (**Ref 1**)

1.5.3 Waste minimisation and waste disposal routes

The Inorganics sector is diverse and wastes are very process-specific, but some parts of the sector do generate significant quantities of waste and in most cases they are non-combustable so there are major disposals of waste to landfill. The Landfill Directive reduces the options for disposal of many chemical waste streams so operators must maximise all waste minimisation opportunities and move their waste up the waste hierarchy.

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

1.5.4 Emissions to water

Many inorganic installations have small or easily treatable aqueous waste streams but a number have effluent streams containing more difficult pollutants such as heavy metal compounds or complexes. Where it is not practicable to prevent the generation of these difficult waste water streams in the first place, they need to be segregated and treated separately, before being discharged to communal effluent treatment facilities. Effluent streams specific to individual process are identified in **Section 2.1** and its sub-sections in this Note, and treatment techniques are covered in **Section 2.2.2**. More detail on available techniques is provided in the Waste Water and Waste Gas Treatment BREF, and in other relevant BREFs, where available. (See **Ref 1**)

1.5.5 Odour

Some of the substances produced or used in installations covered by this Note have the odour potential to cause offence to neighbouring communities This is a key issue for some installations, though probably not for the majority in the sector. The issues are covered in the Odour section in this Technical Guidance Note (**Section 2.2.6**) and in more detail in Horizontal Guidance Note H4 covering Odour (see **Ref 22**).

1.5.6 Energy efficiency

Some Inorganics installations are very large users of energy and the direct or indirect release to air of combustion products often is the biggest single environmental impact arising from their production activities - but other installations in the sector are very significant net generators of energy. Most installations will be participants in a Climate Change Agreement or have an Emissions Trading Scheme permit (which, together with basic energy efficiency measures, are generally deemed to meet the PPC requirement to use energy efficiently). However, even at these installations there may be some issues which need to be addressed in the PPC Permitting process. (See **Section 2.7**.)

1.5.7 Noise and vibration

Noise and vibration are constant features of most large volume inorganics plants - from compressors and other machinery, steam relief valves, large combustion units, flares, etc. Guidance is provided in the Noise section in this Technical Guidance Note (**Section 2.9**) and in greater detail in the Horizontal Guidance Note H3 covering Noise (see **Ref 15**).

1.5.8 Chemical analysis and monitoring of emissions

The Inorganics sector is very diverse but even where there are similarities, emissions monitoring has been rather variable within the sector, to date. With national reporting and comparison (via databases like the Pollution Inventory) becoming the norm, it is important that there is consistent measurement of comparable release streams, both in terms of substances monitored and methods of analysis used. Further guidance is being developed but interim guidance is provided in **Section 2.10** - Monitoring - in this Note.

1.6 Summary of emissions

The Inorganic Chemicals sector is very wide and across the sector almost any substance might conceivably be a potential release to any medium. It is considered, therefore, that there is little value in providing a releases summary of the type used in some other sectoral Guidance Notes.

1.7 Technical overview

More than 50 different processes are covered by this Note and it is not possible to provide detailed descriptions of them. Instead, brief outline descriptions and flow diagrams are given for the main Inorganics processes operated in the UK, together with an indication of their main emissions and any the techniques which are special to those processes.

The larger Inorganics processes are continuous and are often co-located on large integrated sites, so that they can beneficially exchange raw materials, products, by-products and wastes. In some cases, the sharing of energy streams and other utilities is the main benefit. They represent a wide range of different chemical processes based on combinations of unit operations. There are, however, several key issues common to many processes such as the control of acid gas and particulates emissions and the minimisation and reuse of wastes.

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

1.8 Economics

Inorganic processes, even the large volume ones, are not part of a single homogeneous industry and there is a wide range of process types and of plant sizes. A few of the large volume products - for example, ammonia, sulphuric and nitric acids, ammonium nitrate, chlor-alkali, titanium dioxide, sodium carbonate - can be described as industrial sub-sectors with some comparable characteristics (albeit mostly internal to that sub-sector) but the majority of inorganic chemicals are manufactured in Europe on a relatively small scale by just one to three companies, with most of the competition coming from outside the EU. For most of these processes, apart from the application of abatement systems to remove common pollutants like particulates or acid gases, there are few financial characteristics which can meaningfully be used across the board to compare them - and even then, whilst certain abatement techniques are common to many processes, the large variations in scale and technical duty can result in very large differences in cost per tonne of product or cost per tonne of pollution abated.

This variability makes prescriptive approaches to the identification of what is BAT very difficult but a number of issues related to the industry structure, the product market and the operating conditions of the sector can be highlighted. Frequently, individual processes are part of a larger operation, so there needs to be careful consideration of the whole range of associated operations when assessing cost impacts.

SMEs are important in the sector so to avoid over-burdening small companies, in particular, careful consideration needs to be given to making environmental improvements cost-effective in relation to the environmental benefits to be gained. Increasingly there is foreign ownership of companies in the sector so another factor which may need to be considered is the choice that international companies have regarding investment -and changes in ownership and management structures lead to changes in attitudes to environmental performance - both positive and negative - and these present opportunities for review of environmental performance (by both operators and Regulators).

Apart from smaller niche products, new inorganics installations are likely to be few and far between and most developments will continue to be extensions to existing plants - so the opportunities provided by such developments should be used to review BAT overall and to implement environmental improvements.

Economic issues specific to some of the sub-sectors are noted below. In the absence of BREFs covering most of the Inorganics sector, the information has been taken from IPC Technical Guidance Notes S2 4.03 and S2 4.04 (**Ref 21**).

1.8.1 Sub-sectors

1.8.1.1 Sulphuric acid and related businesses

The current UK market for sulphuric acid is now a little over 1Mtpa - which represents a very sizeable fall from the 4Mtpa market of the 1970s and 80s. This is mainly due to the cessation of phosphoric acid manufacture and decline of other UK fertilisers production, to lower steel production and a general decline in tonnage chemical manufacture which used sulphuric acid. The number of sulphuric acid manufacturers in the UK has declined to just 3, which together produce around a half of UK demand, the other half being imported as 96% acid (mainly from European smelter plants).

One producer obtains most of its SO_2 raw material by thermal destruction of waste acid from methacrylate production and recycles the majority of its acid and oleum to that co-located methacrylates plant; the others are sulphur burners and produce a significant proportion of their outputs as specialist grades of sulphuric acid or 100% sulphur dioxide or trioxide.

Basic 96% or 98% sulphuric acid is a mature commodity, most of which is now satisfied by-product acid from non-ferrous metal production overseas. UK production has moved towards specific sulphuric acid-related products where importation is expensive or impractical, or to production which meets a specific local need.

1.8.1.2 Ammonia production

Ammonia production in the UK is around 1Mtpa and is undertaken by two foreign companies on 4 separate sites. On the 3 largest sites, ammonia production is closely integrated with nitric acid and ammonium nitrate production - and the ammonia business environment is closely allied to that of the nitric acid and ammonium nitrate businesses. As well as nitrate outlets, ammonia is used in significant quantities in the manufacture of other chemicals and polymer intermediates, and the overall market is balanced by imports.

1.8.1.3 Nitric acid and related businesses

Nitric acid production in the UK is similar in size to sulphuric acid production, and again there are just 3 or 4 producers (none of which are UK companies). Most weak nitric acid is used captively to manufacture fertilisers (mainly granular ammonium nitrate) or intermediates in the manufacture of polyurethanes or fibres, but it is also sold for the manufacture of explosives and other chemicals, and for the surface treatment of metals. Most concentrated (i.e 96%) nitric acid is also for merchant sales.

1.8.1.4 Fertilizer business

Western European fertilizer production and consumption have declined by at least a third since the end of the 1980s. The availability of cheaper imported fertlizers, particularly ammonium nitrate and particularly from Russia and former Eastern Bloc countries, had a disastrous effect on prices with consequential closure of a significant proportion of EU production capacity. It is possible that the European fertiliser environment is now stabilising, albeit at a lower demand level, and that the oversupply situation is improving - but it is not absolutely clear.

Within the UK, the fertilizer industry comprises 3 large overseas-owned concerns that manufacture granular ammonium nitrate and related fertilizers, together with a small number of independent blenders or granulators. With fertilizer consumption estimated to fall at a rate of 0.5% - 1%pa to around 1.3Mtpa (as N) by 2007, it seems unlikely that much new investment is likely to occur in the near future - though there will probably be opportunities for environmental improvements as existing plant is revamped.

1.8.1.5 Chlorine and sodium hydroxide

Chlorine is a large-volume commodity chemical for which prices fluctuate widely. The chlorine production business is cyclical (recently around 8 year cycles) and the business cycle is fairly closely related to the manufacture of vinyl chloride monomer (VCM), its largest end-user, and thus to the demand for PVC.

A major feature of the industry is that a tonne of chlorine is always co-produced with 1.2 tonne of equally valuable caustic soda. Thus when one is in demand and its price is high, the other has to be produced and outlets found for it - so its price is usually low. For this reason, it is not so much the fluctuating price of chlorine which dictates the profitability of the business as the combined prices of chlorine and sodium hydroxide - and this tends to fluctuate rather less.

Electricity costs are typically over half of total manufacturing costs for chlor-alkali producers, whereas feedstock costs are usually less than 15%. In recent times, as a result of electricity deregulation and a significant increase in generation from natural gas, electricity costs in the UK have been amongst the lowest in Europe so the UK chlor-alkali industry has been reasonably competitive within European markets - but the forecasts for future electricity pricing and perhaps, therefore, for chlor-alkali businesses, are not so sanguine.

Apart from the major end-use, the manufacture of PVC plastic, there are a number of other significant users of chlorine plus many small-volume applications within industry. Many of the other uses for chlorine have already declined under environmental pressure, e.g. chlorine for pulp and paper bleaching, chlorinated solvent manufacture, hypochlorite bleaches, chlorine in water treatment and, of course, the manufacture of CFCs and other ozone-depleting substances. However, other uses for chlorine within the chemical industry are likely to show above-average growth, e.g. for titanium dioxide, phosgene, propylene oxide, pharmaceuticals and other organics.

In the UK, sodium hydroxide is used in most industrial sectors as well as being one of the major raw materials in many chemical production processes, but in a global context there are a few major uses, such as in the processing of aluminium ore, which can have a significant effect on prices.

The major debate within the chlor-alkali industry worldwide concerns the replacement of mercury electrolytic cells by membrane or diaphragm cells for environmental reasons. Europe has a large proportion of its capacity based on mercury cells and in the UK, apart from 2 or 3 small membrane cell-rooms, all the 700-800 ktpa of chlorine production is now via mercury cells and, as a proportion of chlor-alkali capacity, mercury-based production has actually risen over the last decade. There is a Recommendation from PARCOM (the Paris Convention, now known as OSPAR) to phase out the use of mercury cells by 2010 but, in practice, the replacement of mercury cells in many European countries has been patchy over the last 15-20 years. The Chlor-alkali BREF states that BAT for new plant is the use of membrane cells and, whilst mercury losses to the environment have been significantly reduced by recently-installed abatement and recovery techniques, none of the 3 primary UK producers has yet undertaken to replace existing cell-rooms with membrane units. Their argument has been, hitherto, that the environmental gain is too small for the capital cost entailed (estimated to be around £300 million for the currently installed capacity).

1.8.1.6 Titanium dioxide manufacture

Titanium dioxide is a widely used pigment, with demand closely linked to growth in housing, the automobile and the coatings industries. It is a typical commodity product with major product price and profitability cycles. The cycles are not always in phase with the overall chemicals industry cycle. In recent cycles, good profitability in mid/ late 1980s led to major new-plant investment, which resulted in overcapacity and lower profitability in the early 1990s and, since then, prices and profitability have oscillated. Some planned new plants, particularly in the US, have been delayed or abandoned and some capacity, particularly sulphate-route, has been removed. In Europe most investment has been to boost output by debottle necking existing facilities by introducing new process technology, catalysts, etc.

On a worldwide basis, the sulphate process has dropped from about two-thirds of total capacity in 1985 to nearer one-third now. It is likely that there will always be a residual market for the sulphate-based TiO_2, where there is still demand for the anatase pigment, but markets for their by-product materials (i.e. ferric sulphate and gypsum) will be an important factor.

1.8.2 Costs of pollution abatement

This industry sector covers a range of different processes with different scales of operation - ranging from small-scale batch facilities through to large continuous manufacturing processes. A very wide range of chemical species with differing physical, chemical and lexicological properties are stored, handled and processed. The costs of abatement techniques vary widely according to process duty and site-specific factors. The following information is therefore very general and relate to data collected in 1997. The costs of abatement on individual installations may be significantly different and to demonstrate BAT, it is the operator’s responsibility to develop robust cost estimates that correspond to its own specific processes and circumstances.

1.8.2.1 Particulate matter

Within the inorganic chemicals industry one of the main abatement issues is that of abatement of particulate matter from gaseous streams. There are a number of alternative technologies available (as described in **Section 2.2** and in a number of BREFs (**Ref 1**)) and the choice will depend upon technical, site-specific and economic considerations. A number of appropriate criteria for consideration are given below:

- volumetric flowrate, temperature and humidity;
- size and nature of the particulates;
- presence of other chemical species;
- required efficiency of particulate removal;
- waste disposal considerations;
- control and monitoring requirements;
- utility requirements; and
- space availability and civil engineering work.

One of the main factors in the choice of technique is that the efficiency of particulate capture varies enormously with particulate size for some techniques - but for most techniques, the capital cost of particulate matter abatement is very dependent on the flowrate (**Figure 1.1**) and, generally, rather less dependent on the loading.

Different techniques have differing energy requirements. **Figure 1.2** gives a general comparison of the total annualised costs of the same types of equipment.

Figure 1.1: Installed cost of equipment for capture of Particulates

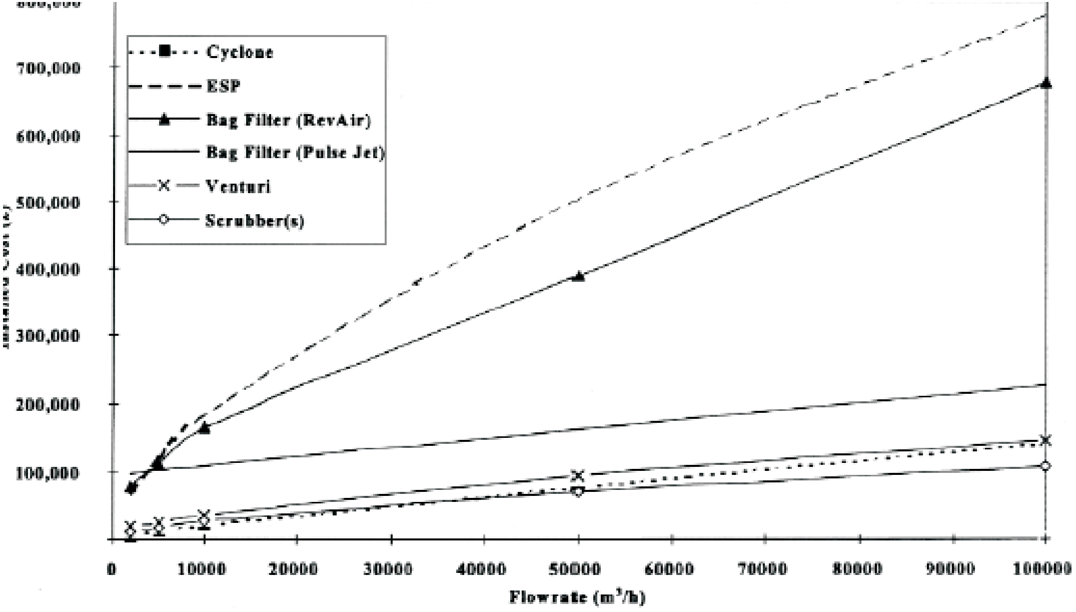
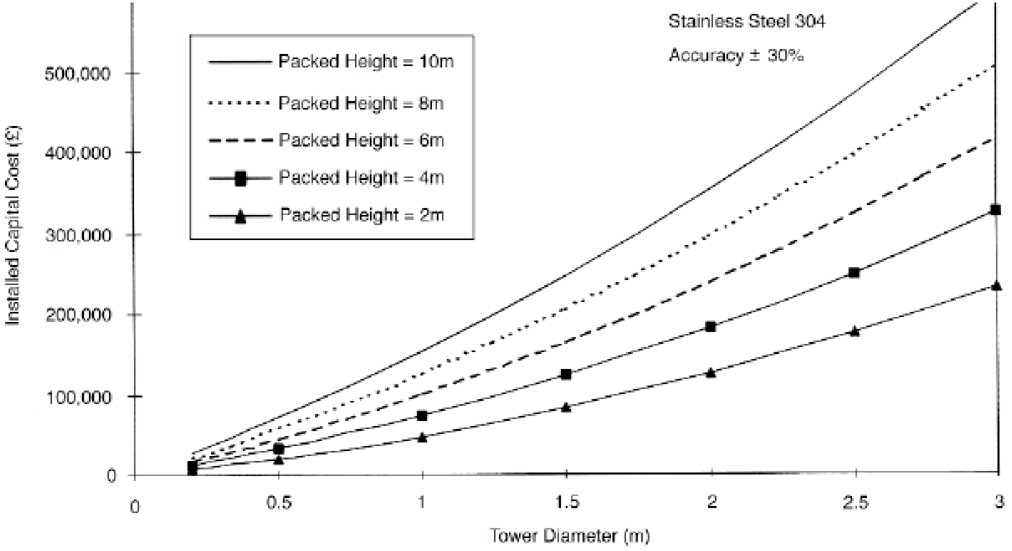


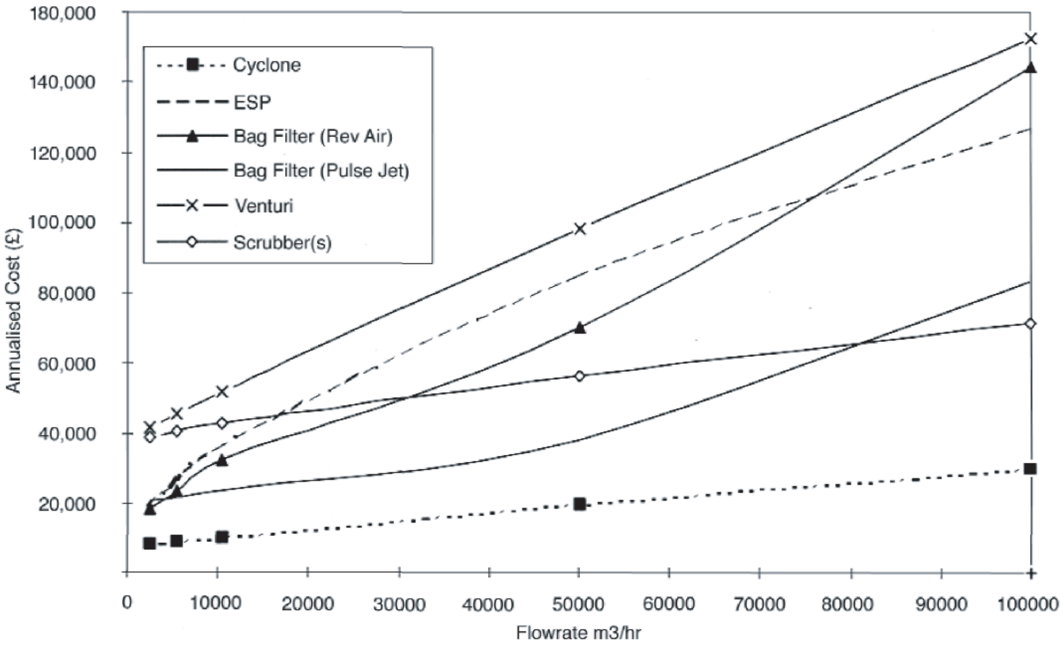
Figure 1.2: Total annualised costs for capture of Particulates



1.8.2.2 Gas scrubbing

Scrubbing techniques are widely used in the sector for gaseous pollutants but the diverse nature of the pollutants, the scrubbing medium and operating conditions make it impracticable to give typical annualised costs so **Figure 1.3** shows just the installed capital costs for various sizes of a common type of scrubbing equipment constructed in stainless steel.

Figure 1.3: Installed cost of stainless steel scrubbers



1.8.2.3 Volatile organic compounds

Some Inorganics processes have significant releases of organic compounds to air. The capital cost s of different types of VOC abatement are a function of gas flowrate, the properties and concentration of the VOCs concerned, specific site issues, and issues relating to the partyicular technique. The costs given in **Table 1.1** are approximate costs for non-halogenated VOCs. Equipment to treat halogenated VOCs is generally more expensive owing to the larger sizing of equipment required by some of the technologies or to the materials of construction required by others.

Table 1.1: Examples of VOC Abatement techniques - approximate costs

Technique	Flow (m^3/hr)	Capital costs (£)	Operating costs (£/annum)	Annualised Total costs (£/annum)
Adsorption - canister	200	1000	100	260
Adsorption - regenerable fixed bed	10000	900000	26000	173000
Absorption	5000	550000	17000	107000
Condensation - refrigerant	1000	400000	13000	7800
Condensation - cryogenic	200	200000	--	--
Thermal oxidiser	25500	750000	278000	400000
Catalytic oxidiser	34000	750000	300000	420000
Biological oxidiser	3600	300000	5000	54000

1.8.2.4 Water treatment

Aqueous effluent from Inorganics activities can be very varied and often are passed to a site waste-water treatment plant where a mixture of wastes are treated so incremental costs arising from the subject processes are difficult to identify. Major components of waste steams are metal compounds and other species specific to the Inorganics process, and specific treatment techniques will be required. Some relative comparative costs for a 100 m^3/day facility are shown as examples in **Table 1.2**.

Table 1.2: Examples of specialised waste-water treatment - approximate costs.

Technique	Capital costs (£)	Operating costs (£/annum)	Annualised total cost (£/annum)
PAC	3500	800	1300
GAC	1900	3000	6200
Chemical coagulation	120000	2500	22300
Ozone	150000	5800	30000
Air stripping	10500	--	17000

Some waste streams contains high concentrations of organics or other compounds which are similarly oxidisable and which need to be almost completely removed. **Table 1.3** illustrates the relative costs of alternative (or additional) techniques to treat effluent with a high organic (or oxidisable) content. The flow is 5 m^3/h with an organics content of 5000 mg/l.

Table 1.3: Cost of Treatment of a high-organic or oxidisable aqueous effluent

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

2 Techniques for pollution control

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

Summarised indicative BAT requirements are shown in the "BAT boxes", the heading of each BAT box indicating which BAT issues are being addressed. In addition, the sections immediately prior to the BAT boxes cover the background and detail on which those summary requirements have been based. Together these reflect the requirements for information laid out in the Regulations, **so issues raised in the BAT box or in the introductory section ahead of the BAT box both need to be addressed in any assessment of BAT.**

Although referred to as indicative BAT requirements, they also cover the other requirements of the PPC Regulations and those of other Regulations such as the Waste Management Licensing Regulations (see Appendix 2 for equivalent legislation in Scotland and Northern Ireland) and the Groundwater Regulations, insofar as they are relevant to PPC permitting. Where EU Directives such as the Waste Incineration Directive and the Large Combustion Plant Directive are implemented through the PPC regime, the requirements of these Directives may also be included.

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

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

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

- The possibility of preventing the release of harmful substances by changing materials or processes (see **Section 2.1**), preventing releases of water altogether (see **Section 2.2.2**), and preventing waste emissions by reuse or recovery, have all been considered, and
- Where prevention is not practicable, that emissions that may cause harm have been minimised and no significant pollution will result.

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

2.1 In-process controls

2.1.1 Environmental Performance Indicators

The following sections outline briefly some of the processes in the Inorganic Chemicals Sector, and indicate the potential waste streams emanating from each. Control of those emissions and waste streams is described in **Section 2.2**.

2.1.2 Sulphuric acid, sulphur trioxide, sulphur dioxide and sulphites

2.1.2.1 Manufacture of sulphuric acid from sulphur

Most commercial processes for sulphuric acid manufacture in the UK use the "contact process" for the catalytic oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) in a multi-stage reactor (known as the converter).

The contact process can be carried out with either single absorption or double absorption of the sulphur trioxide. Double absorption results in increased process efficiency and therefore reduced losses of unconverted sulphur dioxide to the atmosphere.

The sulphur dioxide feed can originate from a variety of sources, including smelting and waste acid destruction processes, but the majority of sulphur dioxide is produced in the UK from elemental sulphur. A significant amount is produced from spent sulphuric acid but none is now produced from smelting operations.

2.1.2.1.1 Process chemistry

The manufacture of sulphuric acid from sulphur by the contact process takes place in three stages:

Sulphur is burnt in an excess of dried air to form sulphur dioxide. This is then further oxidised to sulphur trioxide in a multi-stage catalytic converter. The sulphur trioxide is absorbed in approx. 98% sulphuric acid, where it reacts with water to form more sulphuric acid. All three reactions are exothermic.

1 $S + O_2 \text{ ----> } SO_2$

2 $2\ SO_2 + O_2 \text{ <===> } 2\ SO_3$

3 $SO_3 + H_2O \text{ ----> } H_2SO_4$

The combustion reaction (1) is essentially irreversible. The ignition temperature of pure sulphur is about 260 ºC but typical combustion chamber temperatures are around 1000 ºC. This temperature is too high for the conversion of sulphur dioxide to sulphur trioxide and so the gas stream is cooled before it enters the converter.

Oxidation of sulphur dioxide (2) is a reversible reaction and occurs at an appreciable rate at temperatures above 380 ºC in the presence of a suitable vanadium pentoxide catalyst. Reactor bed temperatures are generally controlled between 380 ºC and 620 ºC, the equilibrium composition at each bed outlet being influenced by temperature, SO_2 concentration and the ratio of oxygen to sulphur dioxide. Maintaining the correct conditions is essential for obtaining maximum conversion.

The rate of SO_3 absorption, reaction (3), is greatest in 98 - 99% sulphuric acid.

2.1.2.1.2 Process description - Single absorption

The Single Absorption process is illustrated in **Figure 2.1**

Water vapour in the process air to the plant is removed in a drying tower circulating concentrated sulphuric acid (96-98%). SO_3 reacts with water vapour to produce very fine acid particles (< 10 micron diameter) so air drying is essential to minimise subsequent mist formation. The pressure is boosted to between 0.3 and 0.7 barg by the main blower and the dry air is fed to the sulphur furnace where liquid sulphur is sprayed and burnt to form sulphur dioxide.

The furnace exhaust gases are cooled from about 1000 ºC to the required converter inlet temperature (in the range 400 - 500 ºC), normally by a steam-raising waste-heat boiler.

The converter normally consists of four catalytic beds in which the sulphur dioxide is oxidised to sulphur trioxide. To prevent the conversion becoming equilibrium-limited, heat of reaction has to be removed after each stage so that the process gas re-enters the subsequent bed at 400 - 450 ºC. This is usually achieved with waste-heat boilers but in Single-absorption plants, temperature control is sometimes effected by the introduction of dilution air between the beds of the converter.

The sulphur-trioxide-rich gas is then passed through the absorption tower where the sulphur trioxide is absorbed in 98 - 99% sulphuric acid.

The conversion efficiency depends on the inlet gas composition and the operating temperatures within the converter. For a Single-absorption sulphur-burning plant the typical conversion efficiency is in the range 98 - 98.5%. This performance is readily achievable when there is steady-state operation and with an O_2:SO_x ratio of about 1.3 - 1.6 (i.e. 8 - 9% vol SO_2 in the feed gas). On some plants, for reasons of capital cost and energy recovery, the SO_2 concentration ex-burner and inlet to the 1st catalyst bed is higher than this and additional "dilution" air is added to the gas entering the second and subsequent stages of the converter progressively to reduce the concentration to the equivalent of 8 - 9% vol SO_2.

The Single-absorption process is utilised in older existing plants but is only favoured now where the available SO_2 concentration is low and variable, e.g. some types of metallurgical plants.

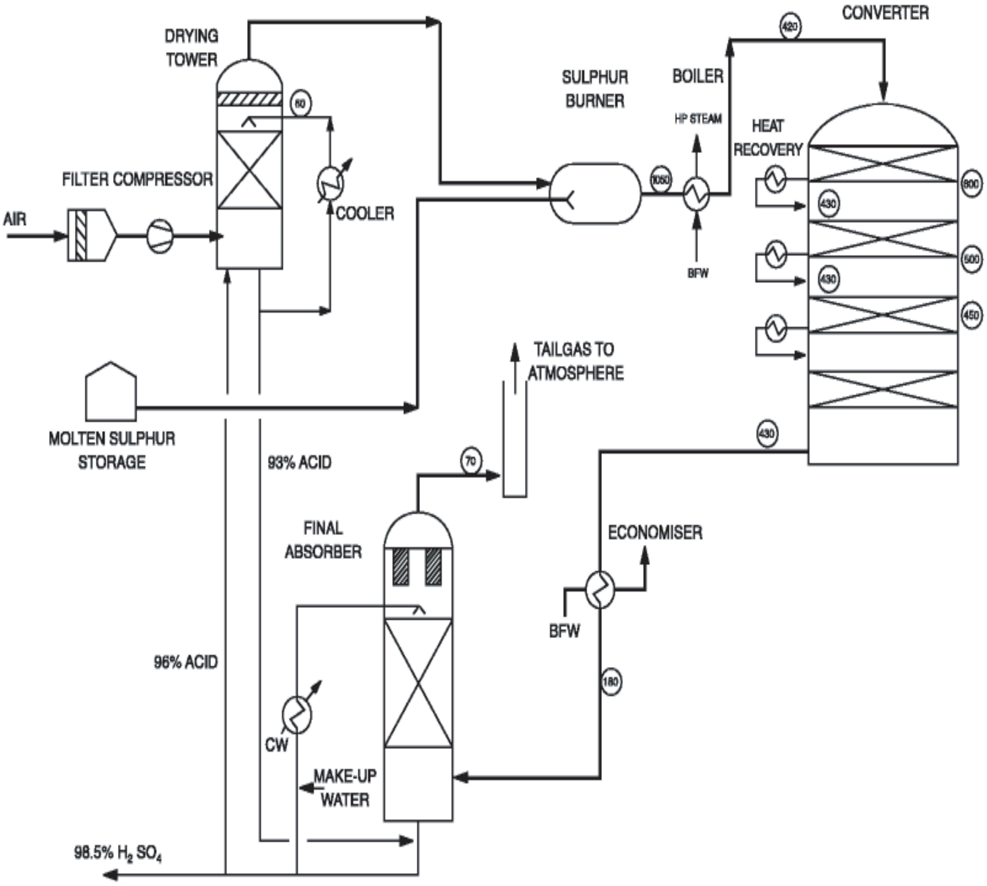


Figure 2.1: Sulphuric acid from sulphur - Single absorption

2.1.2.1.3 Process description - Double absorption

The process is similar to that of Single-absorption except that sometimes there are 5 catalyst stages and, fundamentally, after the second or third catalyst bed the gas is cooled and passed to an intermediate absorber (98.5 - 99% sulphuric acid) which extracts the sulphur trioxide that has been formed (see **Figure 2.2**).

The SO_3-free gas is then reheated and returned to the subsequent stages of the reactor. The greatly enhanced O_2:SO_x ratio alters the equilibrium conditions with the result that there is a significant increase in overall sulphur dioxide oxidation when compared to the Single-absorption process. After the second conversion the process gas is cooled and passed to the final absorber which also operates at 98 - 98.5%for extraction of the SO_3, with the tail gas containing the residual SO_2 released from the plant stack. The two absorber systems and the drying tower system (and oleum absorber, if present) are usually operated with large recycle flows of acid between them in order to maximise SO_2-stripping and recycle to the converter, and to optimise dilution and cooling duties across the Acid plant, both of which are crucial for acid quality and for maximum SO_3 absorption.

The double absorption process was developed to give conversion efficiencies over 99.5% and therefore much reduced sulphur dioxide outlet concentrations in releases to air. It can operate with an O_2:SO_2 ratio of 1.0 (i.e. 10.5% SO_2 in the feed gas on a sulphur-burning plant) or even a little less, and can be made to achieve >99.8% conversion.

For new sulphuric acid plant, particularly sulphur-burners, double absorption is the preferred technique.

For upgrading existing plant it is recognised that several options exist which can achieve similar emission performance to the preferred option above, and may be equally acceptable for the purposes of upgrading. They include:

- employ a high- performance catalyst;
- install extra catalyst beds;
- employ a tail gas scrubbing technique;
- upgrade from single absorption to double absorption; or,
- employ a pressure technique to increase the sulphur trioxide at equilibrium further towards 100% conversion;

The upgrading of a plant to double-absorption would involve, as a minimum:

- breaking in to the converter shell to extract and re-inject reaction gas, after SO_3 absorption;
- rearranging the heat recovery circuit on the converter to provide high-grade heat for heating the return gas from the intermediate absorber;
- addition of a new absorber and associated cooling system;
- modifying the acid circuits to optimise product acid/ water balance; and
- modification or replacement of the air compressor to cover the increased pressure drop through the extra equipment.

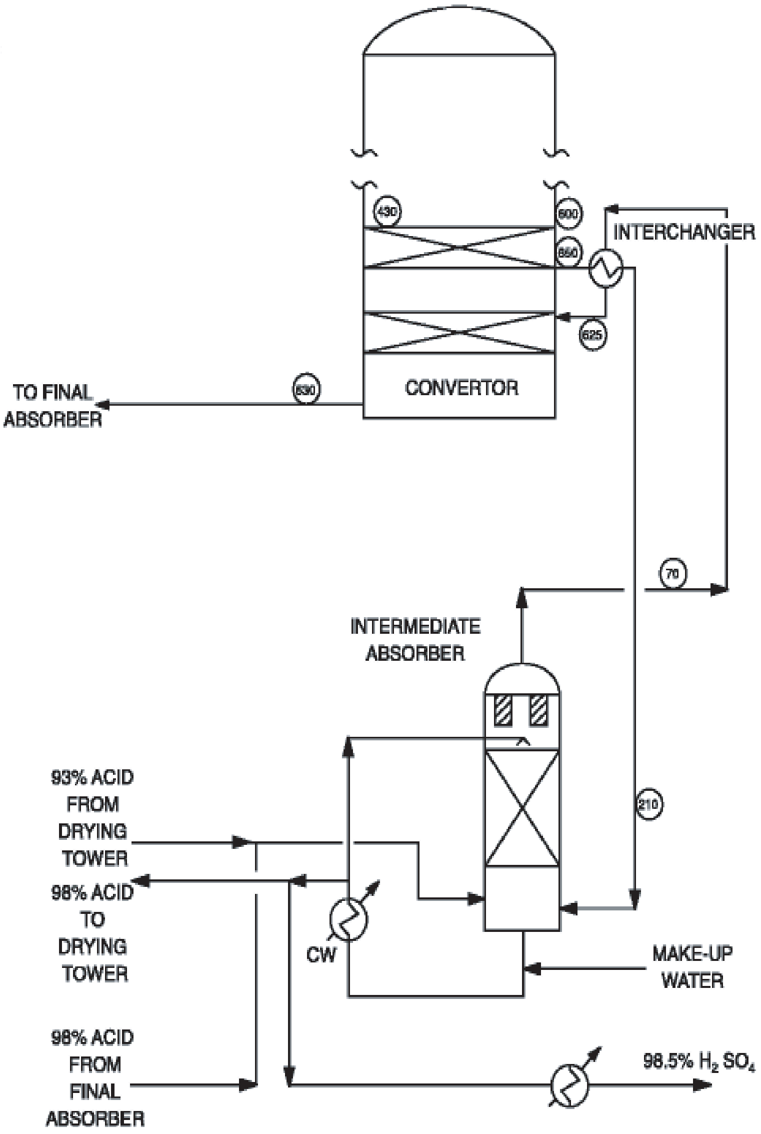


Figure 2.2: Sulphuric acid from sulphur -Intermediate absorption

2.1.2.1.4 Combustion of sulphur

(a) Sulphur storage and handling

Solid sulphur, particularly in dust form, presents a significant fire risk because of its low ignition temperature and its tendency to develop static charges. Consequently sulphur is handled in its molten form wherever possible. Liquid sulphur storage tanks are insulated, steam-heated and typically constructed from mild steel with submerged anti-syphon fill-lines to minimise splashing, agitation, the release of hydrogen sulphide and the build-up of static charges. Storage tanks should be fitted with a steam quench and should also have adequate roof vents to provide natural draught ventilation of hydrogen sulphide gas. All sources of ignition should be excluded from the immediate vicinity of the tanks.

Sulphur, particularly that recovered from oil- or gas-refining processes, may contain very significant levels of hydrogen sulphide; in these cases a closed ventilation system fitted with a caustic scrubber may be required.

All molten sulphur lines and spray nozzles must be steam-jacketed to hold the sulphur temperature above 120 ºC and preferably near 140 ºC.

Where liquid sulphur is transferred to and from storage, careful operation of flexible hoses and temporary connectors is advised to prevent release.

Where solid sulphur is delivered or ensues from leaks/ spillage, the propensity for sulphur fires to start requires that the sulphur be removed to a suitable repository. Suitable methods of detection and extinguishing such fires should be employed.

(b) Sulphur furnace

A typical sulphur furnace consists of a horizontal, brick-lined combustion chamber with dried air and molten sulphur introduced at one end. Some furnace designs contain baffles or secondary air inlets to promote mixing and effective combustion.

The temperature of gas leaving the sulphur burner is a good indication of sulphur dioxide concentration, e.g. 970 ºC corresponds to about 10 vol% SO_2 and 1130 ºC to 12 vol% SO_2.

At high flame temperatures, small amounts of NO_X are formed and some furnaces are operated at near stoichiometric sulphur/oxygen ratios to minimise NO_X formation, (the extra air required for conversion of SO_2 to SO_3 by-passes the furnace). The NO_X tends to accumulate in the acid that is collected in the mist eliminators downstream of the final sulphur trioxide absorber.

The sulphur furnace normally operates under positive pressure conditions corresponding to the discharge head of the main acid plant blower.

2.1.2.1.5 Catalytic converter

A classic approach to high total conversion efficiencies involves a series of catalyst beds with intermediate cooling by either heat exchange or air dilution. In double absorption, the removal of sulphur trioxide in the intermediate stage forces a higher equilibrium curve to be established and higher conversions are achievable.

Figure 2.3 illustrates how SO_2 conversion efficiency changes between beds and between single and double absorption.

Commercially available catalysts are based on vanadium pentoxide and alkali metal sulphates as the active agents and the normal potassium-based catalysts allow the reaction to proceed rapidly at temperatures above 410 ºC 'Low bite' catalysts containing caesium (or other alkali metals) have a lower ignition temperature of about 380 ºC. As the forward reaction is exothermic and the temperature increases progressively through each bed of catalyst, it is the exit temperature which determines the equilibrium composition that can be approached for each bed. Therefore the lower the temperature at which the reaction can be made to start, the higher the SO_3 composition will be in the equilibrium mixture at the correspondingly lower exit temperature. Caesium catalysts used in the later (i.e. lower temperature) beds particularly after intermediate absorption, have demonstrated the potential for increased overall conversion and lower SO_2 releases to air - albeit at higher cost.

(a) Preheating

It is during the period shortly after start-up that the sulphuric acid plant is most likely to release higher-than normal concentrations of SO_x so the converter and absorber systems should be as close to normal operating temperatures as possible before SO_2 is introduced.

The catalyst beds in the converter may be preheated directly with combustion gases from the burning of oil, or indirectly with hot (usually dried) air from oil- or gas-fired preheaters, or a combination of both techniques.

The aim is to have as many of the four (or 5) catalyst beds at temperatures at which the catalyst will 'strike' before SO_2 is admitted. While the optimum arrangement will vary between plants, it is unlikely that a satisfactory start-up will result if fewer than two beds can 'strike' immediately and the later beds are more than 100 ºC below 'strike' temperature beforehand - and no attempt to start-up at below-par temperatures should be made.

The advantages of indirect preheating are that the air is clean and dry and can therefore be passed through the final absorption and demister sections without dilution of the acid or risk of fouling the acid or demisters with the products of incomplete combustion. The tail gas is then emitted from the plant stack essentially free of mist and SO_2. The disadvantages of indirect preheating are higher capital cost and, generally, a longer preheating phase. The justification will be influenced by the frequency of start-ups which require preheating of the converter.

Direct preheating (which is on sulphur-burning plants usually involves oil being burnt in the sulphur furnace instead of sulphur) has the advantage of not requiring much additional equipment but the disadvantage of exposing the catalyst (and its associated SO_3) to the products of combustion, i.e. water and hydrocarbons/ smoke. Catalyst damage by water is avoided either by direct firing through the plant with an excess of air so that water concentration is minimised, or by indirectly heating the catalyst with dry air until the catalyst temperature is above the sulphuric acid dew-point (typically 100 ºC+) and then firing through directly. With some designs of sulphur furnace the indirect phase can be accomplished by using the furnace as a recuperator that is alternatively heated by direct firing and then cooled by dry preheating air passing to the converter.

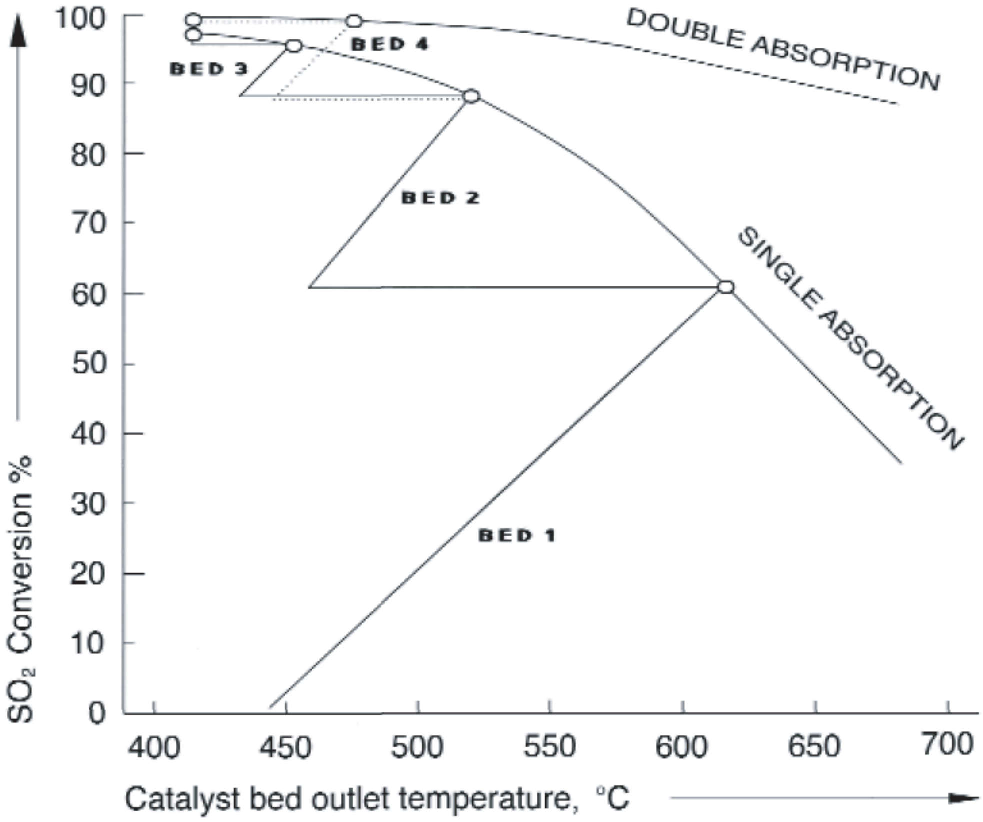


Figure 2.3: Comparison of single absorption and double absorption processes

A further disadvantage of direct firing is that the fuel may contain sulphur and therefore will add to the SO_2 discharge during start-up. Low-sulphur fuel oil or fuel gas is to be preferred to minimise the additional SO_2 release. During the final stages of direct firing it is usually necessary to pass the gases through the absorber.

Another disadvantage of direct preheating concerns the effect of the combustion products on the absorption/ demister sections of the plant. To avoid dilution and smoke contamination of the absorber acid and fouling of the demister elements, it is common to exhaust the preheating gases after the fourth catalyst bed and before the final absorber. This is satisfactory until the temperature of the fourth bed reaches a point where it is no longer able to retain or absorb SO_3 and a visible emission results. Further preheating can then only take place if the tail gas is routed through the absorber section - with the attendant disadvantages noted above. This period of operation should be kept to a minimum. Indirect heating is the preferred technique.

On double-absorption plants, the intermediate absorption section is usually by-passed during preheating to maximise heat transfer to catalyst in the second conversion stage. This re-routing of the preheating gas can be accomplished using large valves or dampers, but on larger plants in particular gas-tight re-routing is more commonly achieved by the insertion of spectacle plates and blanks. The reverse operation must be carried out to restore the normal gas path before the plant is started up.

The total time for preheating can be as much as three days, depending upon the type and capacity of the preheating equipment and on the type and size of the converter. It is important to attain the maximum practicable temperatures in the third and fourth (and fifth) beds if start-up emissions of SO_2 are to be minimised.

Continuous monitoring of SO_2 in the vent gas is a powerful tool with which to control progress through the start-up period. Besides the progressive adjustment to inlet temperatures to the catalyst beds as the plant approaches normal working temperatures, the air flow and SO_2 gas strength can be frequently adjusted to optimise exothermic heat input into the beds and SO_2 concentration in the tail gas.

The plant tail gas often contains a small amount of SO_3 for a short period after start-up and is therefore visible as a misty plume. To minimise the period of plume visibility the absorbers need to be at or close to their normal absorption strength (97.5-99%) at start-up and be brought up to normal temperature (>70 ºC as quickly as possible. The acid strength is usually maintained during the preheating stage by import of fresh 98% acid or oleum.

Preheating may be unnecessary during 'hot' start-ups. Hot start-up occurs either during planned or unplanned maintenance, or during plant trips. Provided the shut-down lasts less than 2-3 days, then enough heat should be retained within the plant and converter beds to permit the re-introduction of sulphur burning without prior preheating of the beds. For pre-planned short shut-downs, one means to maintain the bed temperatures is to allow them to rise prior to coming off-line. The small increase in emissions due to reduced conversion efficiency can be more than offset by the reduced emissions upon starting the converter up again. Applicants should outline the nature of such practices, so that sufficient flexibility is given in the Permit to allow use of such techniques where they are considered to be BAT.

(b) Converter temperatures

It is normal to be able to maintain very steady conditions when operating a sulphur-burning sulphuric acid plant.

Duplicate inlet and outlet thermocouples should be provided, and the temperatures within the catalyst mass should also be recorded. Regular calibration checks should be carried out and faulty thermocouples replaced as part of the ongoing maintenance programme. Pressure drops should be routinely measured and with good records, it is possible to monitor the gradual but inevitable deterioration in the condition (both pressure drops and activity) of the catalyst in each pass. Depending on the sulphur source, it is normal practice for the catalyst in the first pass to be sieved every two years to remove ash and catalyst dust with the bed being topped-up with new material. The other beds are likely to be screened less frequently and are more likely to be screened and partially replaced to improve the activity The spent catalyst is either removed by the catalyst supplier for recycling or sent to a landfill site for disposal.

2.1.2.1.6 Feed conditions

There should be sufficient instrumentation available at the central control panel to provide the operators with accurate information on the following plant feed conditions:

- sulphur feed rate or sulphur pump speed;
- air flow-rate or discharge head of the main blower; and
- sulphur dioxide content of the feed gas to the converter or sulphur furnace temperature.

The plant should be fitted with safety interlocks that prevent continued operation upon equipment failure, e.g. the sulphur feed pump is tripped on loss of acid circulation on an absorber or dryer or on reduction of the main airflow. These should be detected through measurement of flow or pressure rather than just indirectly such as through a 'motor failed' signal.

2.1.2.1.7 Sulphur trioxide absorption

Sulphuric acid exerts a complex vapour pressure consisting of a combination of sulphuric acid, water and sulphur trioxide. The total vapour pressure is a minimum when the acid concentration is between 98 and 99%. This is the optimum concentration for the absorption of sulphur trioxide.

At lower concentrations, the water vapour pressure of the acid is high enough to combine with the sulphur trioxide to form a sub-micron acid mist that is not absorbed in the acid. While at higher concentrations, the sulphur trioxide vapour pressure is sufficient to prevent complete absorption.

(a) Mist formation in absorption towers

Acid mist is visible and easily detected by both the operator and the public. The avoidance of mist depends on operation within carefully controlled limits and therefore the use of properly calibrated sensors and the inclusion of associated control loops. Minimisation of levels of water vapour throughout the plant is important.

The absorption efficiency of sulphur trioxide is highest when the acid concentration is between 98 and 99%. When properly operated, the absorption tower of a sulphuric acid plant is extremely efficient, absorbing much more than 99.9% of the sulphur trioxide in the inlet gas. However, when this efficiency falls off, due to an upset temperature or concentration condition, even small quantities of sulphur trioxide passing through the absorber will react with moisture in the atmosphere to form a characteristic white and persistent plume of sulphuric acid mist.

Acid droplets entrained in the gas stream at the top of the absorption towers are large, ie 10-100 microns and relatively easy to collect in a mesh-type (impact) separator. However, acid mist is an aerosol of fine particles of sulphuric acid with particle sizes ranging from 10 microns down to 0.07 microns which are much more difficult to collect. The mists are formed either by condensation of sulphuric acid vapour as the gas is cooled or by reaction between sulphur trioxide gas and water vapour at a temperature at which sulphuric acid can condense. Mist formed before the absorption tower passes unchanged through the tower and will pass through a similar packed tower even if irrigated with an alkali. Any aqueous medium makes more mist due to the presence of sulphur trioxide and acid vapour.

(b) Mist collection equipment

High-energy contact devices such as venturi scrubbers will absorb mist, but have not found any extensive application for mist removal from acid plant stacks. High power consumption and the addition of water vapour to the stack gases are the major drawbacks.

Electrostatic precipitation can be used for this duty, but high installation cost is the main objection.

The candle-type filter comprising cylinders of very fine compacted fibres - glass in the case of sulphuric acid mists -is a very effective filtration device that is now widely used in the chemical industry. The highest efficiency candle-type filters (for sub-micron particles) rely on diffusion capture by Brownian motion, but smaller units are designed to collect the slightly larger mist particles by a combination of impact and diffusion. High efficiency candle filters are the usual choice for the final absorber; the same filters or the combination diffusion/impact candle filters should be used after the intermediate absorber to reduce corrosion damage to the plant as well as minimising mist loading.

2.1.2.1.8 Circulating acid system

The operation of absorption and drying towers is closely linked (see **Figure 2.3**) and forms the 'acid system', of which there are two basic types plus variations.

In the double acid system the drying and absorption circuits are operated at different concentrations and the two systems are connected only by the acid cross-bleeds. Thus, 98% acid is cross-fed to the drying circuit where it is diluted to 93-96% by the water absorbed in the drying tower and usually also by continuous water addition. The 93% or 96% acid is then returned to the absorber circuit where it is fortified back to 98% by the absorbed sulphur trioxide. Product acid can be withdrawn from either circuit.

In the single acid system, acid from the absorber tower is cooled and passed over the drying tower. Since the circulation rates are large, the changes in acid concentration are slight and the acid remains essentially at a single concentration.

The drying and absorption towers are packed towers and the acid circulation rates are set to limit the temperature rise of the acid. Heat of absorption is removed in acid coolers, examples of which include water-cooled anodically protected stainless steel shell and tube exchangers, Hastalloy C plate-type coolers, spiral heat exchangers, and PTFE coolers with small-bore tubes, or air-cooled stainless steel exchangers.

The double acid system is more complex in design and operation than its single counterpart, particularly on double-absorption plants where a 3rd slightly different strength may be used on the intermediate absorber circuit. Separating the acid streams keeps them independent of each other. This enables multiple control of acid strengths and temperatures and allows greater flexibility on multi product plants to optimise operation by use of all the available cooling and dilution options.

2.1.2.1.9 Tail gas treatment

There are several viable methods for reduction of SO_2 content in the tail gas from the absorber which may be practicable alternatives to Double Absorption for upgrading of existing single-absorption plants. Some have developed specific to the sulphuric acid industry; others have been used in the desulphurisation of flue gas from power stations. Processes can also be classified as regenerative or non-regenerative.

Regenerative processes are those where the reagent is recovered by further processing and the SO_2 is recovered as either SO_2 or sulphuric acid for return to the sulphuric acid plant. There is no SO_2 recovery or solvent regeneration in non-regenerative processes.

Processes that are available commercially include:
- activated carbon processes that produce dilute sulphuric acid;
- oxidation of SO_2 to SO_3 (and sulphuric acid) by hydrogen peroxide;
- solvent absorption processes with recovery of SO_2 during regeneration of solvent; and
- desulphurisation processes.

(a) Activated carbon processes

Tail gas from the absorber is humidified, with either water or diluted acid. SO_2 is then converted to sulphuric acid by reaction with residual oxygen in the tail gas in an activated carbon bed. Typical recovery efficiencies are in excess of 90% SO_2. There may be water balance problems if the product acid is both too weak and too voluminous to be consumed by the acid plant.

(b) Hydrogen peroxide treatment

In this process hydrogen peroxide is dissolved in 30 - 40% sulphuric acid and then circulated through a scrubber to provide direct contact with the tail gas from the final absorber. The basic reaction is

$SO_2 + H_2O_2$ ----> H2SO4

The process was primarily designed for low SO_2 concentrations, e.g. exit gas from older double-absorption process, as the oxidant is expensive relatively expensive.

(c) Scrubbing processes

SO_2 may also be removed by scrubbing with a range of solvents/ reagents. Dependent on the type of solvent it may be possible to recover SO_2 for recycle to the converter. Solvents in use include:

- Ammonia solution - absorbs SO_2 to produce ammonium bisulphite. SO_2 is recovered by treatment with sulphuric acid. Ammonium sulphate forms as a by-product.
- Sodium sulphite/ sodium hydrogen sulphite - SO_2 is extracted and then released by steam heating. The absorbent is regenerated.
- Other solvents in use include sodium carbonate, citric acid, regenerative amine absorbents and sodium citrate.

Essentially all the processes function in a similar way and involve an absorption/ scrubbing stage followed by a regeneration stage in which the SO_2 is recovered and, where practicable, the solvent is regenerated. Efficiency of SO_2 removal for these processes can be better than 95%.

These 'add-on' processes offer the prospect of being a simpler and cheaper cost than conversion to double absorption, whilst producing a potentially saleable product or by-product. Of these processes, the hydrogen peroxide process is likely to have the lowest capital cost, but highest operating cost due to the price of H_2O_2.

In addition, they may be useful in single or double absorption processes during plant start-up situations to mitigate high SO_2 losses. In such situations the H_2O_2 process may be acceptable.

(d) Gas Desulphurisation

Gas desulphurisation processes range from wet to semi-dry to dry. Wet processes include scrubbing with lime, sodium carbonate or other types of alkaline solutions and usually achieve sulphur dioxide removal efficiencies of better than 90%. However the disadvantages of this type of process are that a water vapour plume is produced from the top of the tail gas stack, a liquid effluent is produced which will need treating before aqueous discharges are made, and the liquid scrubbing agent is relatively expensive.

Semi-dry processes normally involve spraying a slurry of lime, or limestone into the gas. The typical piece of equipment used for this purpose is a spray dryer. The technique typically removes about 85% or more of the SO_2. The heat in the gases evaporates the water in the slurry and leaves a solid gypsum product, which might be of saleable quality. No liquid effluent is produced but a vapour plume would still occur at the top of the tail gas stack. Provision and preparation of the slurry agent is likely to be relatively expensive and it is unlikely that sale of the gypsum would be economic bearing in mind the relatively small volume produced compared for example to that from some coal fired power stations. In addition dust abatement facilities downstream of the spray dryer are likely to be needed.

The dry processes involve injecting lime dust into the gas stream and collecting it, typically on a bag filter system. The chemical reactions between the lime and the sulphur dioxide occurs in the gas stream and over the bag filters. Typical sulphur dioxide removal efficiencies are between 50 and 60% but higher efficiencies are possible. The process offers less benefit than the other two types of processes. However, no vapour plume is produced and there is no liquid effluent, but there are solids to dispose of to landfill.

If a sulphuric acid plant is adjacent to a compound fertilizer plant, then employing ammonia scrubbing will result in an ammonium sulphate effluent that can be fed to the granulator.

The tail gases from a conventional single or double absorption plant are dry because the last stage in the production process involves passing the gas through a circulating stream of concentrated sulphuric acid, which is a very effective drying agent. Therefore the addition of water vapour to the tail gas via the wet and semi-dry processes and its consequential cooling not only results in a stack vapour plume but will also reduce the thermal buoyancy of the plume due to the reduced temperature. As a result re-heating of the treated gas may be needed.

Bearing in mind the potential investment required and disadvantage of these types of scrubbing systems when applied to sulphuric acid plants (they are normally applied to much larger facilities such as power stations), it is unlikely that they will provide cost-effective abatement.

Processes that produce a useful by-product such as gypsum or ammonium sulphate should be required to show that a market can be foreseen for that product. In particular the quantity of gypsum produced by abating sulphuric acid plant emissions is substantially less than from coal-burning power stations. Hence it may be uneconomic to find outlets.

2.1.2.1.10 Pressure process

From the equilibrium relationship, operation of the 'contact' process at elevated pressure will enhance the oxidation of sulphur dioxide to sulphur trioxide.

One potential method of reducing the level of sulphur dioxide emission lies in being able to operate the last stage of conversion in a separate reactor vessel operating at an elevated pressure of 150 kPa(g). A compressor is required to boost the gas through the reactor and associated absorber but a tail gas expander allows 80% energy recovery. This process is potentially a cheaper method of achieving low sulphur dioxide emissions than tail gas scrubbing but it is understood that the technology has yet been proven on a production plant.

2.1.2.1.11 Potential release routes

Releases to air

- Sulphur dioxide and sulphur trioxide from main stack, absorber pump tanks and escapes (e.g. small cracks at converter nozzles).
- Carbon dioxide from combustion plant (e.g. during preheating).
- Nitrogen oxides from main stack.
- Hydrogen sulphide from sulphur storage.

Releases to water

- Small contaminated acidic samples (e.g. stack condensate, decontamination washings, nitrified mist eliminator product).
- Demineralisation plant effluent, boiler blow-down waters and cooling tower purge waters.

Releases to land

- Spent vanadium pentoxide (and alkali-metal sulphate) catalyst.
- Contaminated sulphur and sulphur filter cake.
- Unsaleable scrubber products.

2.1.2.2 Manufacture of sulphuric acid at smelters and ore

roasters

2.1.2.2.1 Introduction

Primary smelting and roasting operations designed for extraction of non-ferrous metals from sulphide ores result in the emission of gases containing sulphur dioxide. Such plants need SO_2 abatement systems and the sulphur dioxide concentration is often sufficiently high for this pollution control facility to consist of a conventional sulphuric acid plant located downstream of gas cleaning plant.

This latter combination is sometimes termed 'wet gas' plant because it includes a purification section in which the feed gas is subjected to a series of dust and mist collection operations which include wet scrubbing.

2.1.2.2.2 Process description

A typical gas clean- up scheme is shown in **Figure 2.4**

Metallurgical off-gases will include:

- particulate, which would clog the first catalyst bed;
- fumes or aerosols of 0.01 to 2 micron diameter formed by condensation of volatile metal compounds (Zn, Pb, Sb, Bi, Cd) and their chlorides, sulphates and oxides)
- volatile metals (As, Se, Hg) and their compounds, which may de-activate the catalyst; and
- gaseous impurities including, for example, SO_3, HCl, HF, CO and CO_2.

These impurities (except CO, CO_2) must be removed for sulphuric acid production.

As a result of the extensive clean-up, the feed gas is cold - 40 ºC compared with around 1000 ºC (before cooling) from sulphur burning. The exothermic heat of conversion from SO_2 to SO_3 has therefore to be used to heat up the feed gas, and little excess may remain for steam generation and energy export. Contact plants cease to be auto-thermal when the sulphur dioxide concentration in the converter feed gas falls below 4.5% (approx), the exact point at which this occurs depending on the amount of detailed design of the plant (and particularly the heat exchange arrangements). In addition, the feed gas from the roasting of some ores can fluctuating widely in flow and SO_2 concentration, often falling below that required to sustain conversion in the catalyst beds. In all these cases additional external pre-heating of the feed is required to maintain adequate conversion.

Lower concentrations of SO_2 (down to 2%) are generally best treated using the single absorption process as slightly more heat of reaction is available for pre-heating the feed, and because the double absorption process is more sensitive to variations in SO_2 concentration. Plant operation has to be carefully monitored and controlled to ensure that, whenever there is a requirement for top-up heat, external pre-heating is quickly brought into service to maintain temperatures in the catalyst beds close to the values required for acceptable conversion.

A recently introduced low-temperature process uses catalytic/ adsorptive activated carbon to convert SO_2 to SO_3, which is periodically flushed from the bed with water as sulphuric acid. High conversion and reduced emissions are said to be possible.

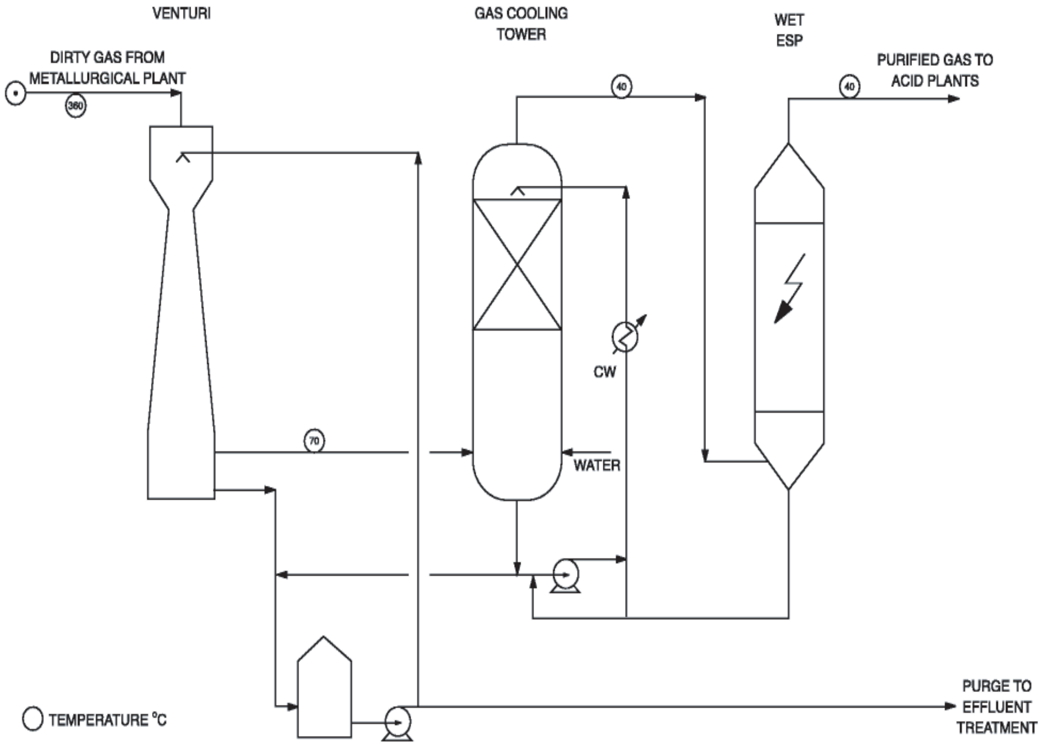


Figure 2.4: Typical flow scheme for SO_2 gas clean-up

The initial dust collection may be achieved in a variable throat venturi scrubber or a dry electrostatic precipitator.

Nickel ores may contain traces of selenium that pass into the exhaust gas as selenium dioxide, which is subsequently removed in the gas scrubber The selenium compounds can be precipitated from the scrubber liquor bleed stream by arranging for a settling tank to be held at weakly acidic conditions of pH4 to pH5.

The aqueous effluent will require treatment (neutralisation and sedimentation) to remove metallic contaminants, acidic, suspended and dissolved components. Where practicable the first sludges separated are recycled to the metallurgical plant for recovery of the metals. Ferrous sulphate, ferric sulphate, lime or caustic soda can be added to the effluent stream to ensure collection of any arsenic that is present.

Traces of mercury fume are present in the exhaust gases from lead/ zinc ore roasting. The mercury removal plant is located after the acid mist precipitators, and consists of a packed tower in which there is a circulating stream of mercuric chloride ($HgCl_2$) solution. This reacts with the mercury vapour in the gas stream to form insoluble mercurous chloride, Hg_2Cl_2 (calomel), which precipitates as yellow-white crystals. Some of the slurry is oxidised with a convenient oxidant such as chlorine gas to regenerate mercuric chloride, which is then returned to the scrubber.

Greater care is necessary when operating a wet gas plant compared with a sulphur-burning one to maintain control of sulphur dioxide and sulphur trioxide emissions.

Some mist is formed in the gas purification section, as the small quantity of sulphur trioxide present in the furnace or roaster exhaust gases reacts with water vapour. Once formed, this mist is very stable and difficult to collect. High-efficiency lead tube electrostatic precipitators can be used for this duty, and it is becoming common practice to provide a two-stage collection system so that some collection is maintained even when one precipitator is out of service. An efficiency of 98.5% can be achieved with a single unit.

The usual criterion of satisfactory mist precipitator performance is that the outlet gas, when viewed through the sight glass provided, is optically clear, corresponding to an outlet loading of about 30 mg of SO_3 per m^3. Operating experience suggests that mist collection is improved if the gas temperature at the inlet of the primary precipitators is significantly above ambient - 40 ºC is a preferred if the plant water balance permits this. The acid mist particles, which act as condensation nuclei, become significantly enlarged as water vapour condenses out of the gas stream.

2.1.2.2.3 Acid bleaching

Acid produced from sinter gas can contain hydrocarbons carried forward in the gas stream from the sinter plant. This carbonaceous material causes the acid to be dark in colour and reduces its commercial value. This coloration can be removed by 'bleaching' the concentrated acid with hydrogen peroxide solution, the bleaching process evolving carbon dioxide and some oxygen. The proportion of peroxide used varies with the initial colour but is of the order of 2 kg H_2O_2 per tonne 96% sulphuric acid produced. The economics of the process are such that the acid should be stripped of SO_2 beforehand to prevent the gas mopping up the expensive peroxide.

The continuous process involves the intimate mixing of the acid and the peroxide through a nozzle followed by retention time in the bleaching tanks of a few hours. Increasing the temperature of the reaction speeds up the bleaching but at the cost of increased peroxide decomposition. Careful control of the hydrogen peroxide injection is required to avoid any excess which could corrode downstream pipework.

2.1.2.2.4 Potential release routes

Releases to air

- Sulphur dioxide and sulphur trioxide from main stack, absorber pump tanks and escapes (e.g. small cracks at converter nozzles).
- Carbon dioxide from combustion plant (and small quantities from bleaching plant).
- Small quantities of nitrogen oxides from main stack.
- Traces of contaminants from the metallurgical plant.

Releases to water

- Gas clean-up produces waters contaminated with minor components from the ore; treatment before consented discharge is necessary but depends on the contaminants present.

Releases to land

- Contaminated tower packing from gas clean- up.
- Spent vanadium pentoxide (and alkali-metal sulphates) catalyst.
- Non-recoverable calomel (mercurous chloride).

2.1.2.3 Manufacture of oleum and sulphur trioxide

2.1.2.3.1 Manufacture of oleum

Oleum, or fuming sulphuric acid, is sulphuric acid containing sulphur trioxide in excess over the formula H2SO4, eg 20% oleum contains 20% sulphur trioxide and 80% sulphuric acid, by weight.

Oleum is normally manufactured with SO_3 concentrations of either 20% or 65% as these strengths have low freezing points (-5 ºC and 0 ºC respectively).

Up to 35% oleum can be made in a single packed tower, while 40% oleum can be generated by two towers in series. In a double-absorption plant the oleum absorber is located before the intermediate absorber. Oleum above 40% is usually produced by mixing liquid SO_3 with low-concentration oleum.

Sulphur trioxide is absorbed in a circulating stream of oleum whose concentration is controlled by cross-bleeding 98+% sulphuric acid from the acid circulation system. Sulphur trioxide absorption is limited by its vapour pressure above the oleum (i.e. by temperature and strength) and remaining SO_3 passes to the intermediate absorber (or sole "98%" absorber on a single absorption plant) for final removal.

Vents and overflow pipework on strong (>25%) oleum storage tanks should not pass directly to atmosphere but should be vented to an SO_3 absorber system, such as a packed tower irrigated with 98% H_2SO4. All vapour lines need to be maintained at 80+ ºC to prevent blockage with solid SO_3 and this requires steam tracing (or high-integrity electric tracing) and lagging, maintained to a very high standard, with temperatures and pressures monitored continuously; all liquid lines need to be maintained above the freezing point of the oleum. Tank high-level control/alarms and overflow protection arrangements must be designed to prevent external spillage, fume emission and moisture ingress - and in-building or double containment storage should be considered for 65% oleum.

Special attention is required in the handling and storage of oleum since exposure to air releases large quantities of fine sulphuric acid mist. Quickly deployable measures to safeguard against such releases should be encouraged. Examples include:

- application of solid absorbent to spillages that are small or in non-bunded areas; and
- use of silicone or similar inert oil to cover large spillages in bunded areas.

2.1.2.3.2 Manufacture of liquid sulphur trioxide

Liquid sulphur trioxide is produced by distilling oleum at 120 - 140 ºC to drive off gaseous sulphur trioxide, which is then condensed at 40 ºC The reduced-strength oleum can be used as a product but is usually returned to the oleum absorber for further sulphur trioxide absorption and re-circulation.

Liquid SO_3 (b.pt. 45 ºC) has to be maintained at temperatures above 30 ºC to prevent the freezing out of polymeric SO_3 (which can only be removed by sublimation at over 70 ºC) so all lines and vessels require lagging and warm-water or electric tracing controlled at around 40 ºC. As with strong oleum systems, all vapour lines must be kept above 80 ºC.

Because of the potential for freezing out of polymeric SO_3 as well as the hazards associated with escapes of liquid or vapour, storage should be double-containment or fully bunded inside a building.

2.1.2.3.3 Potential release routes

Release routes include those for the contact process for the manufacture of sulphuric acid,where applicable, plus:

Releases to air

- Sulphur trioxide (plus some sulphur dioxide) from 98% scrubbers.
- Carbon dioxide in combustion gases, if used for oleum distillation.

Releases to water

- Purges from condenser treated water system.

Releases to land

- Probably none.

2.1.2.4 Manufacture of liquid sulphur dioxide

2.1.2.4.1 Introduction

Liquid sulphur dioxide is manufactured by the following two methods:

- partial condensation; and
- reaction of sulphur trioxide with liquid sulphur.

2.1.2.4.2 Manufacture of liquid SO_2 by partial condensation

The partial condensation method for producing liquid sulphur dioxide operates in association with a sulphuric acid plant, and there are no additional process vents.

The plant inlet gas is a side stream from the sulphur-dioxide-rich gas stream that forms the feed gas stream to a sulphuric acid plant. It is taken from downstream of the waste heat boiler after the sulphur furnace, or after the drying tower on a wet gas plant, and then cooled by exchange with the SO_2 plant tail gas followed by mist filtration to remove any traces of sulphuric acid. Refrigerated cooling down to -65 ºC results in the condensation of much of the sulphur dioxide.

The tail gas from the liquifier contains a significant concentration of uncondensed sulphur dioxide and is normally returned to the sulphuric acid plant and mixed with the converter inlet gas.

2.1.2.4.3 Manufacture of liquid SO_2 by reaction of sulphur trioxide with sulphur

This method is more complex than condensation-liquefaction but it does have the advantage that a very pure product is made and there is not the same cooling requirement. The process is normally integrated with the operation of a concentrated sulphuric acid plant producing oleum and SO_3 as described in **Section 2.1.2.3**.

Molten sulphur is fed continuously with a stoichiometric amount of liquid sulphur trioxide into an agitated reactor containing hot oleum. The heat of reaction is removed by either cooling coils or jacket circulating water at ambient temperature. The gaseous sulphur dioxide produced passes through a bed containing solid sulphur to capture and convert accompanying sulphur trioxide vapour and any residual SO_3 is then removed in a 98% sulphuric acid absorber. The pure SO_2 gas stream is condensed and the liquid product pumped to storage.

The bituminous impurities, which enter the reactor with the sulphur, tend to foam upon sulphonation and must therefore be purged periodically from the system. This is accomplished by removing the reactor contents after about 2000 hours of production, and this weak oleum discharge constitutes the main effluent from the plant.

Sulphur trioxide vents can be routed to any suitable 98% sulphuric acid absorption tower and, like the condensation process, any sulphur dioxide vents can be fed to the converter inlet.

Typically the manufacture of 1 tonne of liquid SO_2 requires 20 kWh of electric power and $30m^3$ of cooling water at 20 ºC

2.1.2.4.4 Potential release routes for SO_2 manufacturing processes

Both processes are normally associated with a sulphuric acid contact process so most releases are integrated with the latter's operation. Generally there are likely to be no additional releases from integrated partial SO_2 condensation but there are a few minor releases from the SO_3 - S process, as follows:

Releases to air

- Release of sulphur oxides upon draining reactor contents.

Releases to water

- Spent reactor contents.
- Sulphuric acid effluent from reactor off-gas purification, if not recycled to the Acid plant.

Releases to land

- Dirty excess sulphur settled out of spent reactor contents.

2.1.2.5 Decomposition of spent sulphuric acid and its recovery

2.1.2.5.1 Introduction

This process can produce sulphuric acid of any desired concentration, including oleum, from almost any waste sulphuric acid stream. The process can be energy-intensive compared with concentration processes, and is generally only used where the waste acid stream is unsuitable for concentration. Regeneration is preferred to disposal.

Sulphuric acid regeneration processes involve decomposing spent sulphuric acid to sulphur dioxide and water, which, after passing through various stages of gas purification, are fed to a conventional contact plant where the sulphur dioxide is oxidised to sulphur trioxide to remake sulphuric acid.

Typical sources of spent acid are from:

- alkylation plants;
- nitration plants;
- acrylonitrile plants; and
- methyl methacrylate plants.

2.1.2.5.2 Process description

The organic content of the acid is effectively incinerated as part of the decomposition process. Unless there is sufficient organic material present in the spent acid, additional fuel is required. The energy required for decomposition may be provided by oil or gas and liquid sulphur or hydrogen sulphide may also be burned in the furnace if the required acid production rate exceeds that of the spent acid. A typical combustion scheme is shown in **Figure 2.5**.

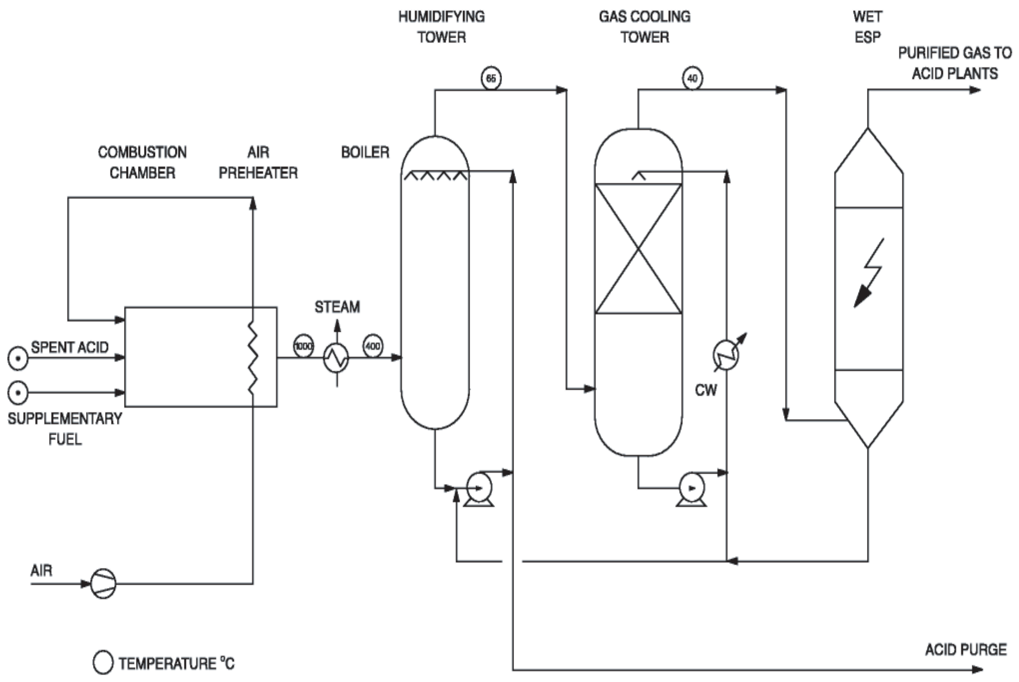


Figure 2.5: Spent acid decomposition and clean-up

The combustion process operates at about 1000 ºC and the quantity of excess air is carefully controlled. Below about 2% free oxygen there is a possibility that some sulphur dioxide will be reduced to sulphur, which can condense at the back end of the furnace and downstream. Besides potential blockage problems, subsequent ignition of this material would result in uncontrolled combustion conditions and fire damage. Too high a free oxygen content, whilst making the plant easier to operate, pushes the equilibrium in the direction of more SO_3 - and this is not wanted at this stage of the process.

A waste heat boiler cools the gases from the furnace to about 350 - 400 ºC, and they then pass to the purification section.

The combustion gases include undecomposed and newly-formed SO_3, particulates and surplus water vapour, all of which must be removed for optimum contact plant operation or to obtain a high-quality acid product.

The purification train humidifies, cools and scrubs the gas of particulates and converts the SO_3 sulphuric acid mist which, if not captured in the towers, is collected in the wet electrostatic precipitator at the end of the section. Although recovery and re-use of the acid may be possible, it is usually mixed with the scrubber acid circulation, the controlled bleed from which is one of the liquid effluents from the process. Typically, 1-1.5% of the feed acid content is lost in this way.

The gas leaving the scrubber is saturated with water, so is cooled further to set the water vapour content such that when it is dried in the Acid plant drying tower, the Acid plant's water balance is maintained. If oleum is being produced in the Acid plant, the reduced water balance will require an even larger gas cooling duty, possibly involving chilled (i.e. refrigerated) water. Condensate from the coolers is often routed back through the scrubber to compensate for the purge required to prevent build-up of solids and acid.

Electrostatic precipitators are used to remove the last traces of sulphuric acid mist and the purified sulphur dioxide stream is converted to sulphuric acid in the same manner as that from metallurgical plants in **Section 2.1.2.2**. - though in this case the strength and variability of the feed gas are almost suitable for the double absorption process.

One process variant is to use oxygen instead of air for the combustion process in the furnace. The furnace is designed to operate at temperatures similar to those in conventional sulphuric acid plant and can accommodate the temperatures associated with oxy-fuel cracking of acid - and the absence of atmospheric nitrogen during combustion ensures that nitrogen oxides are only formed from nitrogen compounds in the waste acid. The use of oxygen reduces the gas volumes by a factor of 2, but apart from the use of much smaller equipment the plant is essentially the same as that described above. Dilution air is fed into the plant at the drying tower so that the concentrations of sulphur dioxide and oxygen in the feed gas to the converter are comparable with sulphur-burning plants.

The water content of the spent acid is critical to the design and operation of the plant. More dilute acids require extra supplementary fuel firing, and hence greater quantities of combustion gases (and reduced SO_2 content). Below 65-70 wt% H_2SO_4 the SO_2 content (less than about 3%) is insufficient to sustain auto-thermal operation of the converter in the acid plant so additional activities like the following have to be undertaken:

- pre-concentration of the spent acid;
- use of oxygen or oxygen-enriched air in the furnace;
- refrigeration of the off-gases to condense more water; and
- preheating of the combustion air to 450-600 ºC

2.1.2.5.3 Potential release routes

These potential release routes include those for the contact process for manufacture of sulphuric acid, as detailed in **Section 2.1.2.1.11** and **Section 2.1.2.2.4**, where applicable.

Releases to air

- Sulphur dioxide and sulphur trioxide from main stack, absorber pump tanks and escapes (e.g. small cracks at converter nozzles).
- Carbon dioxide from combustion activities.
- Small quantities of nitrogen oxides from the main stack.
- Volatile organic compounds (VOCs)

Releases to water

- Acid effluent from gas purification section.

Releases to land

- Spent vanadium pentoxide (and alkali-metal sulphates) catalyst.

2.1.2.6 Recovery of sulphuric acid from nitration processes

2.1.2.6.1 Introduction

A mixture of concentrated sulphuric and nitric acids is used for the nitration of organic compounds such as benzene or toluene to form intermediate compounds which are then used in the manufacture of more complex organic compounds.

The diluted or 'spent' sulphuric acid, which is typically at a concentration of 70-72%, can be concentrated by heating up to 91-93% for re-use - and most impurities that are in the acid tend to be destroyed, eliminated with the evaporated water or are not deleterious if they remain in the product acid.

The most common techniques to regenerate 91-93% acid use a vacuum concentrator or a drum concentrator, and these are suitable for spent acids containing:

- little or no inorganic contaminants, which would otherwise build up on the concentration cycle; and
- less than 10% organic contaminants, which should be volatile or easily oxidised.

2.1.2.6.2 Vacuum concentration

Evaporation under vacuum is a well established chemical engineering technique and allows the use of lower operating temperatures than in the alternative concentration processes. This saves energy and also results in fewer corrosion problems.

The acid is first preheated and passed to a rectification column where the organic contaminants are stripped out of the acid, and a small amount of pre-concentration also takes place. The temperature of acid from the stripping column is then raised to approximately 5 ºC above the acid boiling point at the operating vacuum and injected into the vacuum concentrator. When the acid jet enters the vessel, flash evaporation occurs, with any droplets of acid that are entrained in the departing vapour streams being subsequently disentrained and drained back into the evaporator.

A typical "multi-effect" evaporation scheme is shown in **Figure 2.6**.

The concentration and purification are carried out under forced circulation in two or three vessels arranged in series and operating under vacuum conditions. The evaporators are successively smaller as the acid becomes more concentrated.

Steam is normally used in the acid heaters and there is a water-cooled condenser for the collection of the water vapour evaporated from the acid. The overhead vapour streams from the evaporator vessels and the steam ejector are collected into a common duct, cooled and condensed under a barometric seal. Contaminated condensate is an acidic effluent from the plant and requires neutralisation.

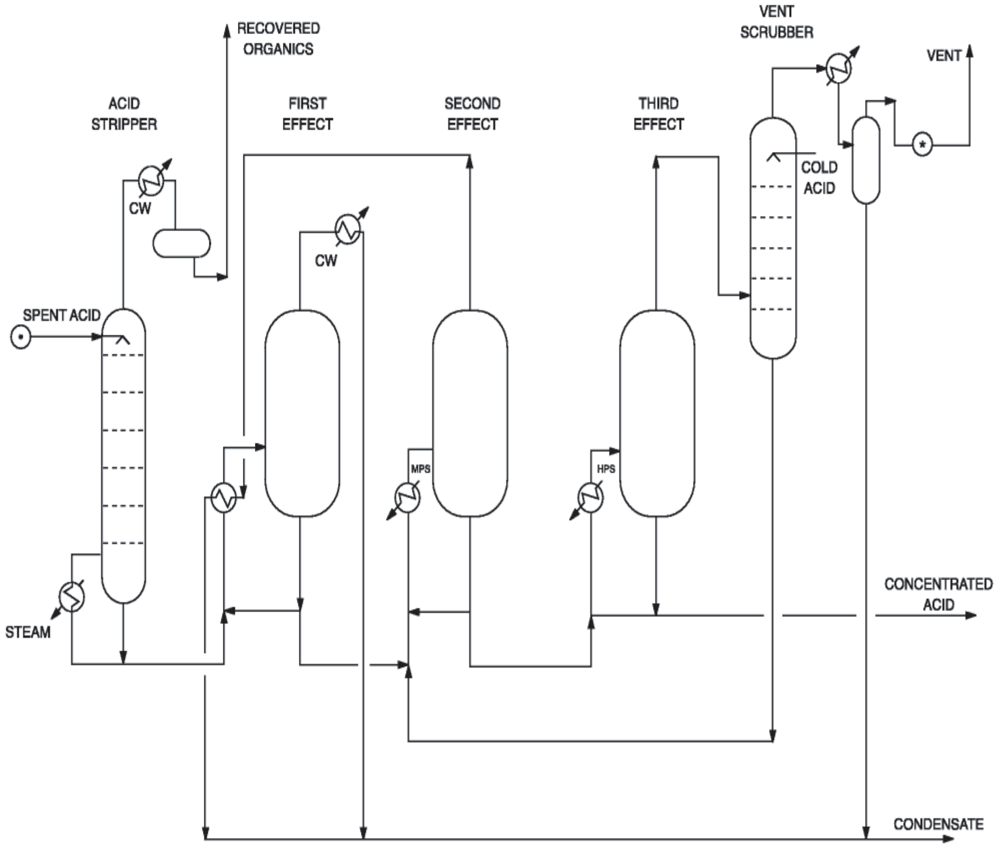


Figure 2.6: Multi-effect evaporation

Any uncondensed vapours and the vents from the pump tanks are scrubbed with water in a small stainless-steel packed column to which air is added to convert some nitrogen monoxide (NO) that is present to nitrogen dioxide (NO_2). Typically, the average NO_X level leaving the vacuum plant is approximately 400-450 mg/ m^3 and has a peak of 1000 mg/ m^3. The required vacuum, less than 4 kPa, is commonly achieved by liquid ring vacuum pumps in combination with steam ejectors.

Extra equipment installed upstream of the concentrator for steam or air stripping of the feed acid should be used to reduce the amount of benzene or other volatile organic compounds (VOCs) that can be present in the discharge gases. The quantity and type of VOCs stripped depends upon the quality of the acid being concentrated. These should be recovered where possible or eliminated, for example by incineration.

Nitric acid may be used as an in situ oxidant to convert the less volatile hydrocarbons to water vapour, CO and CO_2. In the presence of nitric acid, nitrosyl sulphuric acid will form so urea should be added after the nitrosyl sulphuric acid stripping stage to convert it to H_2SO_4, CO_2 and nitrogen. Metal contaminants are not generally removed by the concentration process, though ferrous ion will be oxidised to the ferric form and can be removed as a sludge.

Spent acid concentration may be effective in removing up to 97% or more of the organic material from the recovered acid, but oxidative treatment of the condensate effluent is required to complete the conversion of organics to CO_2 and to achieve acceptable COD levels and eliminate odorous materials prior to discharge.

2.1.2.6.3 Drum concentration

This type of plant generally consists of three vessels in series, in which the acid, flowing through each in turn in one direction, is contacted directly with hot combustion gas at 750 ºC flowing counter-currently. The interconnected vessels are known as the high-, intermediate- and low-stage drums and are lined with lead and bricks. The high-stage drum contacts the combustion gas first with the hot combustion gas being injected below the acid surface through silicon-iron dip pipes. This is the highest temperature, and therefore has the highest concentration. The hot gases pass through the intermediate- and low-stage drums before the exhaust gas is scrubbed and then discharged to atmosphere through the plant stack.

An advantage of the drum concentrator is that it uses combustion gases directly as a source of heat and does not condense the water evaporated, so that its demand on utilities is comparatively small. In addition, the gas stream passing through the drums effectively reduces the partial pressure of water in the atmosphere over the acid and so lowers the apparent boiling point by 50 ºC

Vacuum concentration of sulphuric acid represents the preferred option for this process but Drum concentration will continue to be an acceptable alternative for existing plant providing it meet the same environmental standards as vacuum plant. As with vacuum concentration, this could be accomplished by air stripping the feed acid before concentration, followed by collection or destruction of the VOCs.

2.1.2.6.4 Potential release routes

Releases to air

- Sulphur dioxide and acid mist from the plant vent stack.
- Uncondensed gaseous effluent from concentrator scrubbers containing nitrogen monoxide, nitrogen dioxide and volatile organic compounds.
- Carbon dioxide from combustion plant.

Releases to water

- Acidic effluent containing benzene and nitrobenzene from concentrator scrubbers.

Releases to land

- Where effluent treatment is required, or ferrous ion is present in the spent acid, then a landfill sludge will arise.

2.1.2.7 Manufacture of alkali-metal and ammonium sulphites

2.1.2.7.1 Introduction

Sodium, potassium and ammonium sulphites are consumed in large quantities in the food, paper, offshore drilling and photographic industries. The manufacture of these bulk chemicals, as both solid and dissolved products, generally takes place by absorbing sulphur dioxide in the relevant hydroxide.

The generation of the sulphur dioxide depends upon the scale of operation but will normally be via the combustion of sulphur in air. Stand-by supplies and manufacture from imported liquid SO_2 may be encountered. The generation of the sulphur dioxide will be similar to that for sulphuric acid production except that there is no requirement to dry the combustion air. To increase the yield of high-value product and minimise the total SO_2 emission, the concentration of SO_2 in the exit gas should be as close to 21% as practicable.

It is normal to operate the plant under slight vacuum downstream of the sulphur burner. The vacuum is created by the various distribution blowers/ fans and helps to minimise fugitive emissions.

Larger-scale plants will generally be highly integrated. Any back-end clean-up should use an alkaline scrubber system from which the purge can be fed forward into the process for generation of more product. Such plants are prone to water balance problems and difficulties in matching product demand.

The SO_2 released by each system will be different depending upon whether the product is formed under alkaline or acid conditions. For integrated plants, to minimise the duty on a final scrubber, it is best that the low-pH product is formed from the strong gas strength while the alkaline product is formed under the leaner gas conditions further down the absorption series. This permits the exhaust SO_2 from one process to be used in another, thus minimising overall SO_2 emission levels. Typically total sulphur loss should be less than 0.15%.

2.1.2.7.2 Manufacture of sodium metabisulphite

Sodium metabisulphite ($Na_2S_2O_5$) is produced under acid conditions in counter-current absorber/ reactors. Usually two stages are involved operating under slightly acidic conditions (pH 5). The feed liquor contains a mix of virgin sodium hydroxide and sodium sulphite. Sodium metabisulphite has an appreciable SO_2 vapour pressure and therefore the exhaust gas is typically 2-9% SO_2 by volume, dependent on operating conditions.

A slurry of the crystals formed in the reactor is thickened/ centrifuged to give a cake that is flash-dried and bagged. The mother liquor is recycled back to the process.

2.1.2.7.3 Manufacture of sodium sulphite

Sodium sulphite (Na_2SO_3) is inevitably formed as an intermediate in the production of acid sulphites from caustic soda solution under alkaline conditions (pH 12). When required for sale it may be produced by contacting either neat burner gas or the exhaust gas from a metabisulphite plant. This two-stage counter-current operation can reduce the SO_2 strength in the gas to 0.1%.

Sodium sulphite can also be produced from the hydrogen sulphite by adding caustic soda and employing evaporative crystallisation. This method is energy-intensive but offers a method of continued manufacture when the sulphur burner is out of commission. It is also a means to convert excess hydrogen sulphite into saleable product.

2.1.2.7.4 Manufacture of sodium hydrogen sulphite (sodium bisulphite)

Sodium hydrogen sulphite (sodium bisulphite, $NaHSO_3$) often results from SO_2 abatement prior to exhaust to atmosphere. It exerts a higher vapour pressure than sodium sulphite and this requires production to be located earlier in the gas absorption sequence of an integrated plant. Operational advantages exist over the sulphite for use in abatement systems as it removes twice as much SO_2 for the same caustic requirement. It is also more soluble, so allows a more concentrated but solids-free scrubbing system to be used.

Sodium hydrogen sulphite is a product in its own right but integrated plants tend to manufacture it to excess so it is often converted to sodium sulphite or thiosulphate.

2.1.2.7.5 Manufacture of sodium thiosulphate

Sodium thiosulphate ($Na_2S_2O_3$) is made by oxidising sodium sulphite or hydrogen sulphite with excess sulphur. It can therefore utilise excess hydrogen sulphite and has the added advantage that relatively impure sulphur, eg sulphur spillages from other processes, can be used.

Hydrogen sulphide gas is released (which requires absorption) and the product liquor has to be filtered to remove excess sulphur and solid impurities. The filter cake is disposed of to land.

2.1.2.7.6 Manufacture of potassium sulphites

Potassium sulphite (K_2SO_3) is manufactured in a similar way to sodium sulphite, and potassium hydrogen sulphite (potassium bisulphite, $KHSO_3$) is manufactured in a similar way to sodium metabisulphite.

2.1.2.7.7 Manufacture of ammonium hydrogen sulphite (ammonium bi-sulphite)

Ammonium hydrogen sulphite (ammonium bisulphite, ABS, NH_4HSO_3) is manufactured in either single- or double-stage counter-current absorption plant. In the first stage, neat burner gas or other strong SO_2 stream is contacted in a circulation at around pH 5.5 with the sulphite-rich fed forward from the second tower. Ammonia solution is fed into the higher pH circulation of the second stage and reacts with the unabsorbed SO_2 from the first stage. Control of this pH is important - too low and SO_2 will be lost, too high and ammonia will be stripped out and cause deposition fouling downstream.

2.1.2.7.8 Releases from sulphite producing processes

Air pollution abatement technology is generally conventional SO_X scrubbing technology, with the maximum re-use of recovered SO_2. Particulate from the burner and H_2SO_4 mists are removed from the tail gas by high performance glass-fibre mist eliminators or by electrostatic precipitators. The former also extracts ammonia and the latter can produce a weak sulphuric acid product, allowing the possibilities of maximising recycle or acid recovery.

Releases to air

- Sulphur dioxide (and small quantities of H_2SO_4 mist) from vents and tail-gas scrubbers.
- Hydrogen sulphide from thiosulphate reactors and liquid sulphur storage.
- Ammonia from ammonium hydrogen sulphite plants.
- Particulate from material handling and dryers.

Releases to water

- Minor sulphite spillages from all plant.

- Clean-out of vessels and storage tanks.

Releases to land

- Filter cake from sodium thiosulphate plant, chiefly iron oxides and sulphur.

2.1.3 Nitric acid

2.1.3.1 Manufacture of medium-concentration (57-70%) nitric acid

2.1.3.1.1 General

Most commercial manufacture of nitric acid is by means of the ammonia oxidation process, with the majority of plants constructed for the production of medium-concentration acid (57-70 wt%).

There are many variations in the operating details of the plants producing medium-concentration nitric acid by the ammonia oxidation process. However, there are three essential steps that are common to all plants. These are as follows:

- catalytic oxidation of ammonia (NH_3) to nitrogen monoxide (NO);
- oxidation of nitrogen monoxide to the dioxide (NO_2); and
- absorption of the nitrogen dioxide in water to produce medium-concentration nitric acid (HNO3) accompanied by the release of one nitrogen monoxide molecule for every three molecules of NO_2 absorbed.

Low pressure at the ammonia oxidation stage slightly favours more efficient nitrogen monoxide (NO) production, whilst high pressure in the absorption section markedly favours the oxidation of NO to NO_2 and the absorption of NO_2 in water. The design of nitric acid plants has responded to these conflicting requirements by developing along two separate lines - single pressure and dual pressure operation.

The 'single' pressure system operates the ammonia oxidation step at essentially the same pressure as the absorption section with 'low single pressure' plants operating at a pressure below 1.7 barg, 'medium single pressure' plants operating at 3-6.5 barg and 'high single pressure' plants operating above 7.5 barg. The relative simplicity and lower capital requirement of plant operating with the ammonia oxidation stage and acid absorber at a common pressure has found favour in the United States.

In Europe, the 'dual pressure' or 'split pressure' system has developed in which ammonia oxidation is carried out at low pressure (around 1 barg) and NO_2 absorption at medium pressure (2-6.5 barg) or ammonia oxidation is at medium pressure (3-5 barg) and absorption is at high pressure (above 7.5 barg). The more complex dual compression and energy recovery systems are optimised for the thermodynamic and kinetic requirements of both stages in the overall process.

All the main reactions in nitric acid formation are exothermic and, with modern plants requiring to operate at one or more elevated pressures as well, a major proportion of every nitric acid plant is concerned with heat and power recovery.

A nitric acid plant is mainly constructed from stainless steels selected for these specific duties, with nickel alloys, titanium orzirconium used in some of the more hostile environments. In particular, during the heat recovery process, nitric acid will pass through an acid gas dew-point regime. Cooler tubes may be subject to alternate drying/ wetting/ evaporation zones. Corrosion is also more of a problem with higher-pressure plants.

A basic process scheme for producing medium-concentration nitric acid is shown in **Figure 2.7**.

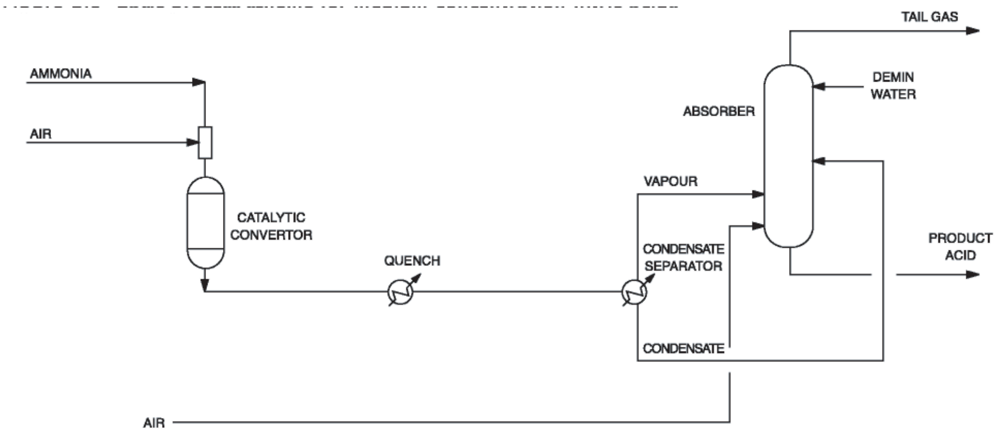


Figure 2.7: Basic process scheme for medium concentration nitric acid plants

2.1.3.1.2 Ammonia oxidation

In the oxidation (combustion) section of nitric acid plants, ammonia is oxidised using air, over a catalyst. During this operation, nitrogen monoxide and water are formed according to the reaction (1):

(1) $4\ NH_3 + 5\ O_2$ --------> $4\ NO + 6\ H_2O$

Simultaneously, nitrogen, nitrous oxide (dinitrogen monoxide) and water can be formed by undesired side reactions:

(2) $4\ NH_3 + 3\ O_2$ ---------> $2\ N_2 + 6\ H_2O$

(3) $4\ NH_3 + 4\ O_2$ ---------> $2\ N_2O + 6\ H_2O$

All three ammonia oxidation reactions are highly exothermic.

Nitrous oxide is not classed as an acid-forming oxide of nitrogen although it has a high global warming potential. It passes with the nitrogen through the absorber to the plant exit stack.

The catalyst typically consists of a woven or knitted gauze formed from wire containing about 90% platinum (the catalyst) alloyed with rhodium and/ or palladium to provide greater strength.

The selectivity of the reaction and the yield of nitrogen monoxide from the catalytic oxidation of ammonia are dependent on temperature and pressure. The lower the temperature and pressure, the higher the yield. Optimum temperatures for catalytic oxidation to NO are in the range 800-950 ºC but, whilst reactors designed for operation at 1 barg can achieve yields of NO from NH_3 of 97-98%, modern plant designs tend to favour operation at 'medium' pressure (3-5 barg) where the yield is around 96%.

Atmospheric pollution, catalyst poisoning and non-ideal gas-flow distribution through the catalyst gauze may progressively reduce the yield by a further 10%.

In the process of the reaction small amounts of the catalyst vaporise. For this reason a collector is sometimes installed below the catalyst to capture this material. Gold or palladium can be used for this purpose to alloy with the platinum and rhodium, allowing initial recovery of 60-80% of the total catalyst losses (see later for overall recovery).

2.1.3.1.3 Oxidation of nitrogen monoxide

The gases cool to 100-200 ºC through the waste heat boiler system and gas-gas heat exchangers, and eventually to around 50 ºC in the cooler-condenser. During cool-down the nitrogen monoxide starts oxidising to nitrogen dioxide according to the reaction (4):

(4) $2\ NO + O_2 <===> 2\ NO_2$

The reaction is exothermic and the conversion of NO to NO_2 increases with falling temperature. Hence the reaction will not be near completion until the gases enter the absorption section.

Oxygen is needed for this reaction to proceed and hence excess air is either introduced with the ammonia feed at the oxidation stage, or is added before the absorption stage to ensure that the waste gas leaving the oxidation stage has an oxygen content of 2 - 4% by volume.

2.1.3.1.4 Reaction of nitrogen dioxide with water

Water produced by ammonia oxidation (reactions (1) to (3)) is condensed in the cooler-condenser, forming a weak acid by the absorption of nitrogen dioxide present, and is then transferred to the absorption tower at the appropriate level for the concentration achieved.

The absorption of the nitrogen dioxide in water and its reaction to nitric acid and nitrogen monoxide take place according to the reaction (5):

(5) $3\ NO_2 + H_2O$ -------- > $2\ HNO_3 + NO$

This reaction is exothermic and the heat released necessitates continuous cooling of the acid within the absorber.

In addition, the undesired reverse of reaction (4) can take place simultaneously in both the gas and liquid phases. Minor formation of nitrous acid can also occur in accordance with equation (6):

(6) $NO(g) + NO_2(g) + H_2O(l)$ --------> $2\ HNO_2$

After most incoming NO_2 has been absorbed in the lower part of the absorber, the critical reaction is again reaction (4), the reaction between residual oxygen and NO molecules liberated from reaction (5). The speed of this reaction is a function of both the oxygen concentration and the square of the NO concentration. As the latter progressively falls, so the oxidation of NO formed in subsequent absorption stages, requires progressively longer residence times.

This reaction is greatly assisted by increased pressure as is the associated absorption of nitrogen dioxide in water. Both reactions are also very dependent on the temperature in the absorber, hence the development of absorption towers operating at pressures above 8 barg and cooled by chilled supply water at temperatures below 10 ºC.

Modern counter-flow absorption towers use high-efficiency tray designs with the spacing between the trays progressively increasing towards the top of the tower to allow for the increasing contact times necessary to oxidise NO to NO_2. Many of the trays are equipped with internal cooling coils for removing the heat of reaction from the absorption of NO_2 with chilled water being circulated through the upper trays and cooling water through the lower ones. Bubble cap trays give better performance but sieve trays are also used. Ceramic packing has been used, in lieu of metal trays, to avoid corrosion problems.

2.1.3.1.5 Typical dual-pressure plant description

A simplified flow diagram is given in **Figure 2.8**.

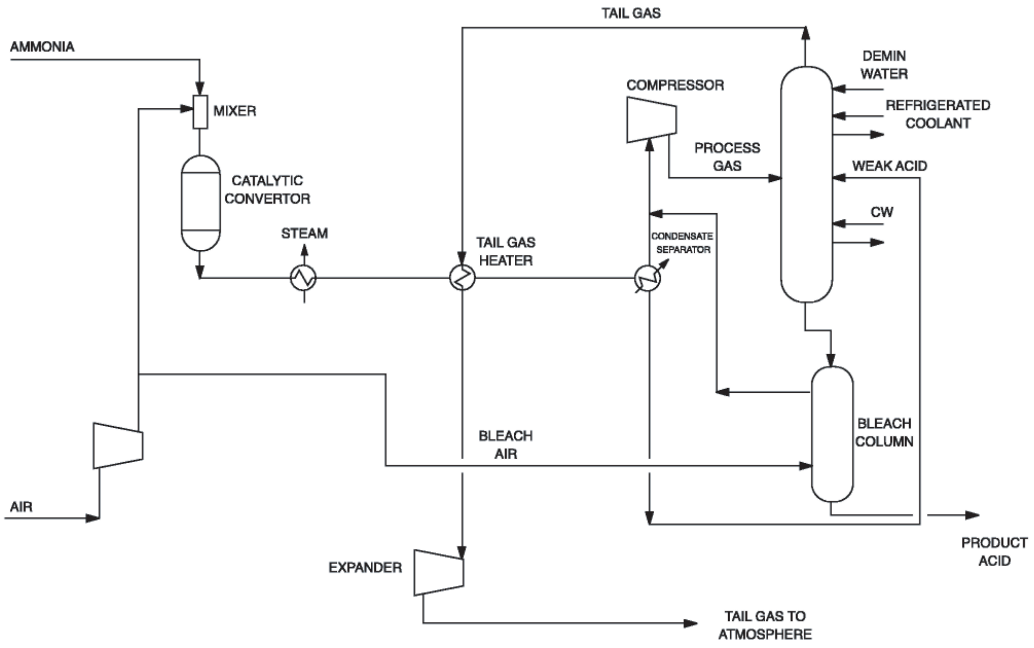


Figure 2.8: Simplified dual pressure flow diagram: medium concentration nitric acid

The ammonia is then mixed with filtered air, which has been compressed and heated. The mixed gases then pass into the catalytic reactor.

Filtering of the two streams is generally carried out separately to minimise the possibility of a preliminary reaction between the ammonia and the air and to prevent catalyst gauze contamination. The reactor is designed to give a uniform distribution of the ammonia/ air mixture over the catalyst gauze.

Maintaining the catalyst at the correct operating temperature is very important. With the air and ammonia temperatures held constant, the catalyst temperature is adjusted by slight changes in the proportion of ammonia to air, ensuring that the lower explosive limit for ammonia in air is not exceeded.

High-purity air and ammonia are essential to maintain good catalyst performance. The life of a catalyst gauze varies from three to five months depending on the process used. The usual impurities are iron (rust) from the ammonia system (unless stainless steel is used), and halides, sulphur and phosphorus from the air supply. Sulphur and phosphorus tend to appear when nitric acid plants are located near to fertilizer manufacturing facilities.

Over the normal life of the catalyst its conversion efficiency falls. This reduced performance is monitored and the catalyst is replaced periodically.

The spent catalyst gauze and collector are sent to the catalyst supplier for recovery of the precious metals and re-manufacture. Sludge recovered from various items of equipment during shutdowns can have a significant metals content and therefore is also sent for metals recovery. Overall, therefore, only a small fraction of the precious metal is lost.

The catalyst is preheated just prior to process ignition, normally using hydrogen burners, which typically raise the temperature of the gauze to between 810 and 940 °C in a period of two minutes.

The catalytic reactor section is typically mounted at the upper end of a vessel, which also contains a number of heat exchangers that form part of an energy recovery system for the process (eg waste heat boiler and superheaters).

After preliminary cooling by these heat exchangers the combustion gases leave the vessel and can be further cooled in additional energy recovery heat exchangers, before final cooling in a cooler-condenser.

Weak nitric acid solution is formed in the cooler-condenser and is separated from the gas and pumped to the equivalent concentration tray in the absorption tower.

In the 'dual pressure' process the 'nitrous' gas leaving the cooler-condenser is compressed to a higher pressure in preparation for the absorption stage.

The heat of compression is removed from the compressed gas stream by gas-gas heat exchangers, which can be part of the process energy recovery system, and the stream enters the base of the absorption tower at around 50 ºC

As the gas flows up through the tower, counter-current to the acid flow, nitrogen dioxide dissolves in the acid forming more nitric acid and releasing nitrogen monoxide. The nitrogen monoxide is re-oxidised in the space between the trays by the excess oxygen that is present. High-quality process water (such as demineralised water or steam condensate) is added to the top of the tower as the absorbent make-up.

The 'tail gas' from the absorption tower is passed via a turbo-expander and other energy recovery equipment to stack. It should be noted that on nitric acid processes the energy recovery systems are usually highly integrated into the overall design of the plant. Figure 2.9 shows a typical arrangement for a turbo-compressor train with energy recovery. Waste heat boiler steam and the tail gas are used to drive turbines to:

- compress the process air; and
- generate surplus electricity where practicable.

Highly integrated energy recovery systems have implications with respect to the use of 'end-of-pipe' abatement techniques (see later section).

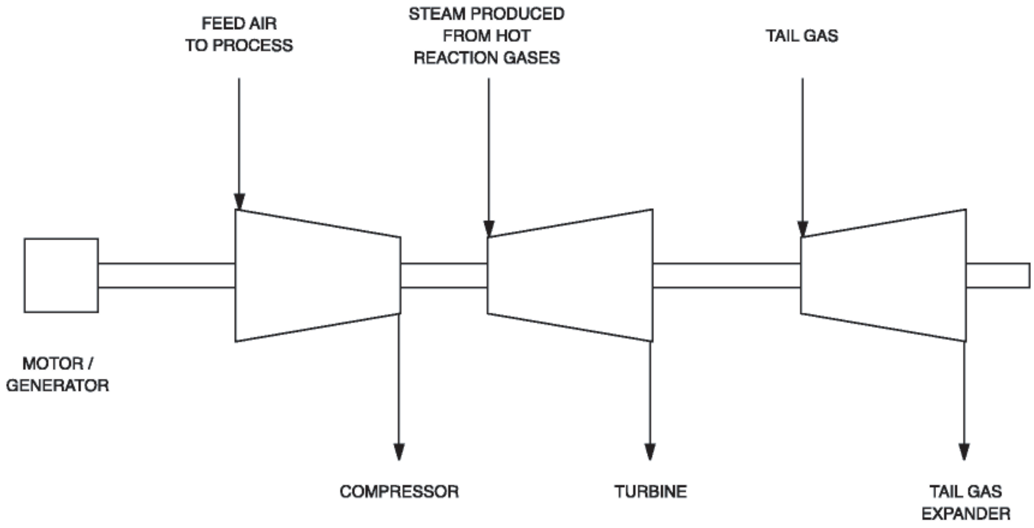


Figure 2.9: Simplified diagram of medium concentration nitric acid integrated drive train

The 'medium-concentration' acid stream leaving the base of the tower is passed to a lower-pressure bleaching column where it is contacted with a counter-current flow of compressed air taken from the air supply going to the ammonia oxidation reactor.

The bleaching column is a stainless steel vessel and is typically no greater than 3 m high and 1 m diameter. It can use either packing or plates and may be integrated with the absorption column.

The air strips the dissolved nitrogen oxides present in the product acid leaving the higher-pressure absorber, thereby producing a colourless, 'bleached', product of strength up to 70%.

The air and stripped nitrogen oxides from the bleaching column are recycled and combined with the main 'nitrous' gas stream leaving the cooler-condenser prior to compression for absorption.

2.1.3.1.6 Single pressure plant description

The single pressure process operates with the same nominal pressure throughout the plant. As such, the only difference between this process and the dual pressure one is that there is no further compression of the 'nitrous' gas mixture leaving the cooler-condenser and the bleaching column. These gases pass directly, upon mixing, to the absorption tower.

2.1.3.1.7 Advantages and disadvantages of the dual pressure process

The reactions occurring in the ammonia oxidation catalytic reactor and the absorption tower are both highly dependent on pressure and temperature (see **Section 2.1.3.1.2** to **Section 2.1.3.1.4**)

At the catalytic reactor, the lower the pressure, the greater the yield of nitrogen monoxide. At the absorption tower, the higher the pressure, the greater the yield of nitric acid. It is clear then that the dual pressure process, which takes advantage of the increased yields at opposing pressures at the reactor and absorption tower, can achieve a greater overall conversion efficiency than the single pressure process.

The disadvantage of the dual pressure process is that it is generally more complex and has therefore a greater capital cost than a single pressure process. However, the energy efficiency of a well designed modern dual pressure plant is comparable with that of single pressure process plants.

2.1.3.1.8 Potential release routes

Releases to air

- Oxides of nitrogen including nitrous oxide from the absorption column via the plant stack, particularly after plant start-up during plant stabilisation.
- Fugitive releases of ammonia from storage, handling and vaporising systems.

Releases to water

- Dilute ammonium nitrite/ nitrate solution from periodic washing (typically once/ day) of the NO_X compressor and from the cooler-condenser drain for a period after plant start-up. On modern plant it may be possible to steam-inject the NO_X compressor to avoid any liquid effluent and also arrange for acidification during start-up to avoid the need to drain the cooler-condenser.
- Aqueous ammonia solution from evaporator blow-down. This can be minimised by steam stripping to recover the ammonia into the process.
- Blow-down of water containing dissolved salts from the steam drum.
- Occasional emissions from the purging and sampling of nitric acid solutions.

Releases to land

- None.

2.1.3.2 Manufacture of high-concentration (95-100%) nitric acid

2.1.3.2.1 Introduction

Because of its low demand, only relatively small-scale processes have been developed for the manufacture of high-concentration nitric acid (95-100 wt %).

The nitric acid produced by the standard ammonia oxidation process is an aqueous solution at a medium concentration of 57-70 wt%. Such concentrations are suitable for the production of ammonium nitrate but, for many organic nitration processes, concentrated or anhydrous nitric acid is required.

Medium-concentration acid cannot be concentrated by simple distillation because nitric acid forms an azeotrope with water at 68 wt%.

Two different routes have been used in the industry to produce concentrated nitric acid, namely:

- extractive distillation; and
- direct processing from ammonia oxidation via superazeotropic acid.

2.1.3.2.2 Extractive distillation using sulphuric acid

Extractive distillation of medium-concentration acid uses a dehydrating agent to break down the azeotrope. The dehydrating agents most commonly used are sulphuric acid and magnesium nitrate.

Depending upon the concentration of the source nitric acid, it is first sent to a pre-concentration tower, where by normal distillation its concentration is increased to close to its azeotropic limit of 68%. The 68% acid is cooled by heat exchange (usually with the acid feed to the pre-concentration tower) and is fed to the concentration tower.

Nitric acid produced in plant using high-pressure absorption of nitrogen dioxide will not normally require this pre-concentration process.

The concentration tower is typically a packed column constructed from glass, with a diameter of 300-900 mm and a total height of up to about 13m.

Either indirect heating or live steam evaporates pure nitric acid from the top section of the tower, where it is in contact with a 96-98% concentrated sulphuric acid solution.

The nitric acid vapour leaving the top of the tower contains small quantities of air and nitrogen oxides and is sent to a final tower, where liquid nitric acid condenses, which is then bleached by air stripping and cooled. This packed tower is fabricated from glass and has similar dimensions to the concentration tower.

The concentrated sulphuric acid fed to the concentration tower descends and becomes more diluted as it does so, reaching a concentration of about 69% in the bottom. It is either removed for de-nitration and subsequent use elsewhere or is re-concentrated and recycled back to the top of the concentration tower.

The tail gas from the final tower is passed first to a water scrubber and where necessary to a NO_X abatement system.

The weak acid solution from the water scrubber should be re-concentrated and re-used.

2.1.3.2.3 Potential release routes using sulphuric acid

Releases to air

- Oxides of nitrogen from the final tower via the stack.
- Sulphuric acid mist from the re-concentration process.

Releases to water

- Weak acid effluent from scrubbers during operation and plant wash-down.

Releases to land

- None.

2.1.3.2.4 Extractive distillation using magnesium nitrate

After pre-concentration if necessary, the 68% acid is fed to a distillation column where it is mixed with a concentrated solution of magnesium nitrate. Nitric acid is vaporised, leaves the top of the tower and is condensed to give the high-concentration acid, with some being returned to the tower as reflux. From the lower part of the tower a dilute nitric-acid-free solution of magnesium nitrate is obtained, which is vacuum-concentrated and returned to the process.

2.1.3.2.5 Potential release routes using magnesium nitrate

Releases to air

- Sulphur dioxide and sulphur trioxide from main stack, absorber pump tanks and escapes (e.g. small cracks at converter nozzles).
- Carbon dioxide from combustion plant (and small quantities from bleaching plant).
- Small quantities of nitrogen oxides from main stack.
- Traces of contaminants from the metallurgical plant.

Releases to water

- Weak nitric acid effluent from plant wash-down.

Releases to land

- None.

2.1.3.2.6 Distillation of superazeotropic acid

Figure 2.10 shows a process flow diagram of the direct concentrated nitric acid route.

Direct processing comprises the novel technology of ammonia oxidation, production of a superazeotropic acid (i.e. 75-80% HNO_3) and its rectification.

Ammonia is oxidised by air in the conventional manner in a reactor at low or near-atmospheric pressure.

The reaction gases, mainly nitrogen monoxide, are cooled to a temperature low enough to condense all the reaction water in the form of weak acid (2% HNO_3). The dry gases enter the oxidation tower, where, in contact with around 60% nitric acid, the nitrogen monoxide reacts with nitric acid in the reverse of the normal nitric acid absorption reactions to produce nitrogen dioxide:

$NO + 2\ HNO_3 <==> 3\ NO_2 + H_2O$

- thereby substantially increasing the nitrogen dioxide concentration in the gas stream.

The depleted nitric acid from the oxidation tower is pumped to the weak-acid absorption tower for re-strengthening to 60%. The enriched NO_2 stream from the oxidation tower is then compressed to about 11 barg, cooled and passed to the strong-acid absorption tower where 68% nitric acid is flowing counter-currently. At this point, the nitrogen dioxide partial pressure in the gas is high enough to produce 80% concentration nitric acid when absorbed in azeotropic nitric acid (68%$HN0_3$).

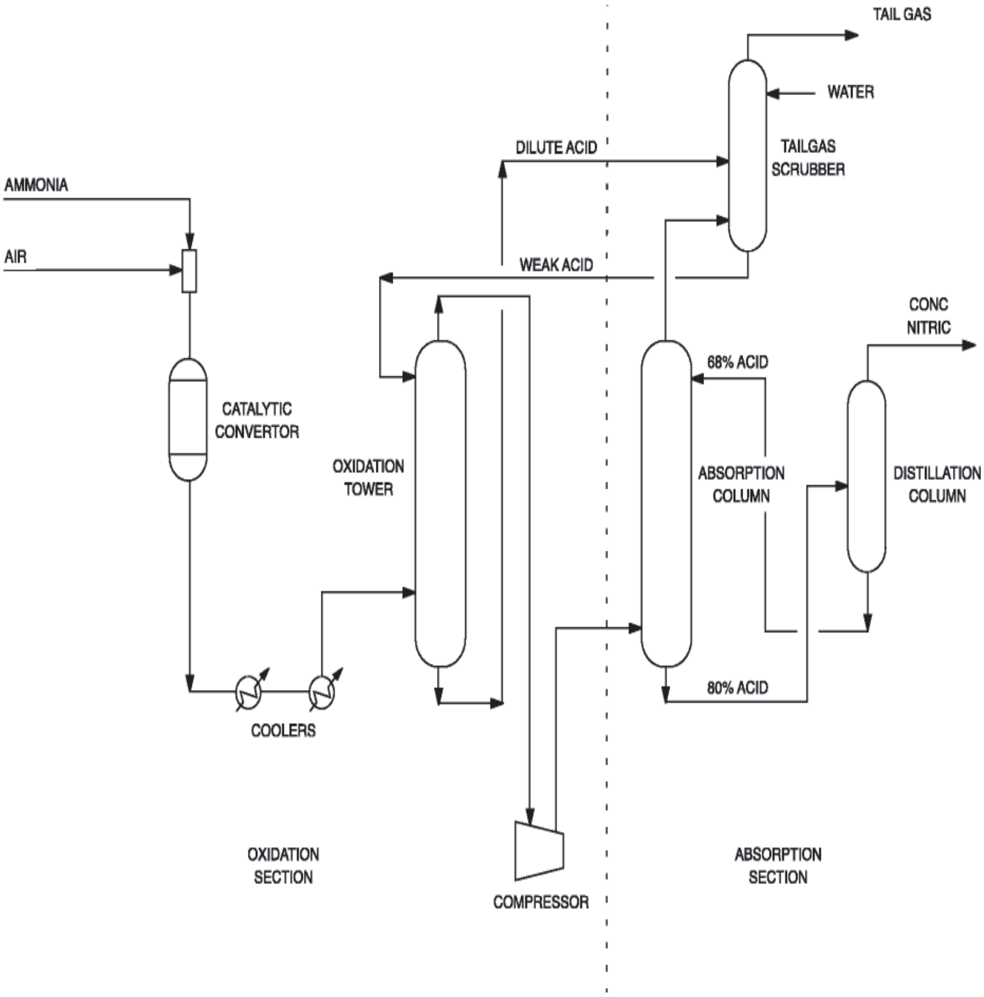


Figure 2.10: Simplified flow diagram: direct route concentrated nitric acid

The resulting superazeotropic acid from the bottom of the tower is then distilled to produce concentrated nitric acid from the top and azeotropic (68%) acid at the bottom, which is recycled back to the absorption stage.

The gases leaving the strong-acid absorption tower contain a high concentration of nitrogen oxides and pass to the weak-acid absorber, which uses water at the top and weak acid from the oxidation tower near the middle, as absorbent to form 60% HNO_3. This nitric acid either becomes the feed to the oxidation tower or is sold as 60% acid.

The tail-gas from the weak-acid absorber passes to the plant exit stack typically via reheat facilities and a turbo-expander and, as it is the product of a high-pressure absorber, it exhausts at a NO_X concentration comparable with the best medium-concentration nitric acid plants.

2.1.3.2.7 Potential release routes from superazeotropic acid

Releases to air

- Oxides of nitrogen from the weak-acid absorption column via the plant stack.

Releases to water

- Weak nitric acid effluent from plant wash-down.

Releases to land

- None.

2.1.3.3 Abatement techniques for nitric acid manufacture

2.1.3.3.1 General

Essentially the only significant process release from a nitric acid manufacturing plant that requires control is the gaseous waste stream from the absorption tower containing the oxides of nitrogen. This stream consists of nitrogen monoxide (NO), nitrogen dioxide (NO_2) and nitrous oxide (N_2O) in various proportions depending upon reactor and absorber performance.

Associated with the nitric acid manufacturing plant will be the ammonia storage and handling systems. Fugitive gaseous ammonia emissions may occur from this equipment, ie from vents and pressure relief devices. The techniques for preventing, or minimising and rendering harmless, releases of ammonia to the environment should include good maintenance and housekeeping practices and leak detection checks. These are covered in **Section 2.2.4**and **Section 2.3** of this Note.

The correct design and operation of the absorption tower are essential in order to limit the concentration of NO_X gases in the tail-gas stream. The important engineering and process parameters are as follows:

- pressure; temperature;
- reaction volume;
- efficiency of the absorption column; and
- partial pressures of nitrogen monoxide and oxygen.

In the absorption stage, high pressures favour the formation of nitrogen dioxide from the monoxide, and also the formation of nitric acid from the dioxide. However, high temperatures inhibit the above conversions.

Consequently if the cooling water exceeds the design temperature due to, for example, the weather conditions, then NO_X emission levels may rise. Plants using chilled water as the cooling medium will obviously have lower and more stable emission levels throughout the year.

Owing to the low solubility of nitrogen monoxide in water and weak nitric acid, a reduction of its partial pressure and thus a reduction of the NO content in the tail gas is impossible without its oxidation to nitrogen dioxide.

For a high conversion of the nitrogen monoxide to the dioxide, a sufficient reaction volume must be available in order to give an adequate residence time for the reaction.

A high contact surface area is required in the absorption tower to give good mass transfer between the liquid and gas phases. Hence column internals of high efficiency, eg sieve trays, have to be provided.

For new small nitric acid plants (say, less than 100 tonne/ day) for which high-pressure compressor, expander or energy recovery equipment is generally less efficient than on a large scale, NO_X releases below 300 mg/ m^3, as NO_2, may be attained more economically by absorber operation at medium pressure (say, 8 barg) and a typical exit concentration of 1200 mg/ m^3 NO_X followed by catalytic reduction.

However, because the reactions necessary for the formation of nitric acid are all reactions that reach an equilibrium, there will always be, even at high pressures and extended residence times, partial pressures of NO and NO_2 in the absorption tower. Therefore, the tail gas from nitric acid plants will always contain small quantities of the NO_X gases.

2.1.3.3.2 Abatement techniques

The techniques that can be applied to both medium- and high-concentration nitric acid plants to abate the releases to the environment of the significant prescribed substances are:

- scrubbing using sodium hydroxide solution;
- extended absorption; and
- non-selective catalytic reduction (NSCR); and
- selective catalytic reduction (SCR).

A summary of the techniques, their impacts and applicability can be found in **Table 2.1**. The above techniques for tail gas treatment require a minimum temperature and pressure. These conditions cannot always be achieved in old nitric acid plants without additional energy input.

Table 2.1: Summary of abatement techniques in nitric acid plants

Control technique	Environmental impacts				Typical NO_X (mg/m^3)	Salient features	Applicability
	Air	Liquid	Solid	Energy			
Molecular sieve	None.	None.	None.	Extra fuel for regeneration.	20	High capital. Cyclic operation. Adsorption	No recent examples of use of process. Good turndown. Can be added easily to existing plant.
Extended Absorption	None.	None.		Pumps and refrigeration	205-410	High capital if retrofitted; Modest capital as integral part of plant design. Limited suitability on LP processes.	Industry standard for new plants.
NSCR	Possible CO. Increased $C0_2$ emissions.	None.	Catalyst disposal.	Increased fuel consumption. Potential for energy recovery.	205	High capital multiple beds with intercooling for low emissions. Removes N_20.	Tending to be superseded by SCR.
SCR	Ammonia slip.	None.	Catalyst disposal.	Small quantity of ammonia required.	100	Does not remove N_20.	Can be added to existing plants.

2.1.3.3.3 Scrubbing using sodium hydroxide solution

By treatment of the tail gas under pressure with sodium hydroxide, nitrogen monoxide and nitrogen dioxide are absorbed in equal volumes reacting to produce sodium nitrite:

$NO + NO_2 < === > N_2O_3$

$N_2O_3 + 2\ NaOH$ -------- > $NaNO_2 + H_2O$

Note: If the molar ratio of NO/ NO_2 is not unity, then the reaction to sodium nitrite is impeded.

A very small amount of surplus nitrogen dioxide will react, but only very slowly, to form sodium nitrate and nitrite according to the equation:

$2\ NO_2 + 2\ NaOH$ --------> $NaNO_2 + NaNO_3 + H_2O$

Surplus nitrogen monoxide does not react with the sodium hydroxide.

Providing the pressure is in excess of 4.5 barg and the NO and NO_2 concentrations are close to parity, this technique is just capable of reducing a tail gas concentration of 1200 mg/ m^3 to 400 mg/ m^3 as NO_2.

The resulting sodium nitrite-nitrate solution from the neutralisation reaction is a liquid effluent and as such may present a disposal problem; hence the alkaline absorption process can only be considered as an abatement option if the effluent can be either utilised (for example as a product) or eliminated without causing further environmental pollution. The system has a further operational disadvantage as sodium nitrate has a tendency to freeze during the winter months. Although present on existing processes this abatement technique is unlikely on its own to be capable of meeting the emission levels achievable by other techniques.

Scrubbing techniques have used a range of chemicals including:

- sulphuric acid;
- ammonia; and
- urea.

2.1.3.3.4 Extended absorption

The absorption efficiency of existing plant may be improved by extending the height of an existing absorption tower, if practicable, or by adding a second tower in series with the existing unit, thus increasing the oxidation volume and number of trays, resulting in more NO_X being recovered as nitric acid and consequently reducing the emission levels.

If extended absorption were to be employed it is most probable that a second absorption tower would be installed, in which case the tail gas from the first tower would be routed to the base of the second tower and flow counter-current to a chilled process water feed to form weak nitric acid. This weak acid would then be cycled to the upper trays of the first tower absorbing the rising NO_X gases from the ammonia oxidation stage and producing the product acid at the tower bottom.

In order to minimise the size of the additional absorption tower the inlet gas would require to be pressurised with additional refrigeration cooling provided for the liquid on the trays.

Tail gas from the second tower may be heated by recuperation from the ammonia oxidation stage and power recovered using a turbo-expander. Extended absorption may offer an environmentally attractive method of meeting NO_X release limits; however considerable integration would be necessary with heat and power recovery to yield a satisfactory operating efficiency.

Other options for extended absorption are:

1. High-pressure absorption at up to 17 bar. To run the whole back end of the plant at pressure will usually require the use of exotic materials of construction. It is claimed that the use of titanium and zirconium can result in cost-effective design.
2. Oxygen injection. Two advantages accrue from the use of increased oxygen as opposed to air in the feed to the bleach column. First, the mass of the tail gas stream is reduced, which reduces the total emission to atmosphere. Secondly, an increase in the partial pressure of oxygen in the system increases the concentration of oxygen in the liquid film. The absorption of NO_X in water to give nitric

acid is the sum of two reactions:

$H_2O + NO + NO_2 <===> 2\ HNO_2$

$3\ HNO_2 <===> 2\ NO + H_2O + HNO_3$

A high concentration of oxygen in the liquid film promotes the direct reaction:

$2\ HNO_2 + O_2 --------> 2HNO_3$

- with a corresponding decrease in NO_X emissions in the tail gas.

Molecular sieve adsorption

The molecular sieve swing adsorption process has been used for controlling emissions. The objections to the process are the high capital and energy costs, and the problems of coupling a cyclic process to a continuous plant operation. As a result no commercial use of this process has been found.

2.1.3.3.5 Non-selective catalytic reduction (NSCR)

In non-selective catalytic reduction (NSCR) processes, the reducing agent reacts not only with the oxygen bound to the nitrogen oxides, but also with free oxygen present in the tail gas. The reducing agent can be hydrogen (possibly from an ammonia plant) and/ or a hydrocarbon (e.g. natural gas or naphtha), but they must be free of sulphur to avoid premature inactivation of the catalysts.

Hydrogen has the advantage of operating at a significantly lower temperature than methane or other hydrocarbons and cannot introduce carbon monoxide or hydrocarbons into the tail gas. However, if, as is sometimes the case, the hydrogen is a by-product from an ammonia plant, the supply may only be available when the ammonia plant is operating. Ammonia plant shut-downs will leave the nitric acid plant without NO_X abatement. Furthermore, any small methane content in the hydrogen will pass out with the tail-gas as the NSCR temperature is too low to react methane with NO_X.

Process description

The tail gas from the absorption tower is preheated by heat exchangers, typically using the hot gases from the ammonia oxidation reactor, to a temperature that is dependent on the design of the plant and the fuel used.

Inlet temperatures for good conversion efficiency and catalyst life are given below for commonly used reducing agents:

- Hydrogen - 200 ºC minimum, typically 300 ºC
- Naphtha, LPG - 350 ºC minimum, typically 450 ºC
- Natural gas - 480 ºC minimum, typically 550 ºC

The reducing gas is mixed with the preheated tail gas stream and a homogeneous mixture is passed into a reactor containing a bed of catalyst. Part of the reducing agent may be used as an intermediate quench.

The catalyst consists of platinum-group metals deposited typically on a ceramic honeycomb. The bed is built up from blocks of catalyst.

The reactions taking place on the catalyst surface can be divided into two groups. The first group of reactions involves the reaction of the fuel with oxygen and nitrogen dioxide, reducing the latter to nitrogen monoxide. These reactions take place first and are sometimes referred to as the "decolorisation" reactions' as fuel merely serves to decolour the plume without reducing the overall NO_X content.

The reactions with different fuels are given below:

Reduction of oxygen:

$CH_4 + 2\ O_2$ -------> $CO_2 + 2\ H_2O$

$2\ H_2 + O_2$ --------> $2\ H_2O$

$2\ C_4H_{10} + 13\ O_2$ --------> $8\ CO_2 + 10\ H_2O$

Reduction of nitrogen dioxide:

$CH_4 + 4\ NO_2$ --------> $CO_2 + 2\ H_2O + 4\ NO$

$H_2 + NO_2$ ----------> $H_2O + NO$

$C_4H_{10} + 13\ NO_2$ ---------> $4\ CO_2 + 5\ H_2O + 13\ NO$

The second group of reactions do not commence until reducing conditions have been achieved. This is when all the oxygen in the tail gas has reacted with the fuel. These are sometimes referred to as the "abatement reactions"

Reduction of nitrogen monoxide (nitric oxide):

$CH_4 + 4\ NO$ --------> $CO_2 + 2\ H_2O + 2\ N_2$

$2\ H_2 + 2\ NO$ --------> $2\ H_2O + N_2$

$2\ C_4H_{10} + 26\ NO$ ---------> $8\ CO_2 + 10\ H_2O + 13\ N_2$

Reduction of dinitrogen monoxide (nitrous oxide):

$CH_4 + 4\ N_2O$ -------> $CO_2 + 2\ H_2O + 4\ N_2$

H2 + N_2O --------> $H_2O + N_2$

$C_4H_{10} + 13N_2O$ --------> $4\ CO_2 + 5\ H_2O + 13\ N_2$

An excess of fuel is necessary to ensure reducing conditions. The gases leaving the catalyst reactor will contain substantially reduced concentrations of nitrogen oxides and oxygen and will consist predominantly of nitrogen gas and water vapour.

Typically, conversion efficiencies are about 90% for the NO_X gases and 70% for nitrous oxide, though under pilot plant trials conversion efficiencies of 90% have been achieved for nitrous oxide.

The reaction of the fuel gas with the oxygen in the tail gas is an exothermic reaction and the gas leaves the catalyst at an elevated temperature. The temperature rise is proportional to the oxygen content of the tail gas but varies according to the pressure and temperature of the reaction. As a general rule the following temperature rises can be used for each 1% of oxygen that is burnt with the named fuel:

- Hydrogen160 ºC
- Methane, naphtha, butane, propane130 ºC

This temperature rise puts a limitation on the maximum amount of oxygen that can be removed on a single pass. This can be calculated by subtracting the inlet temperature required with the chosen fuel from the maximum permissible operating temperature, typically 750 ºC and dividing by the temperature rise obtained if 1% of oxygen were burnt with that fuel. For example, with hydrogen fuel and inlet temperature of 200 ºC the maximum temperature rise allowable is 550 ºC and the maximum oxygen reduction is 3.4%.

Two stages of catalytic treatment are generally only required when methane is the fuel because methane requires the highest catalytic operating temperature. Even so, when two stages are used an intercooler is not usually necessary. It is avoided by admitting the total fuel requirement before the first stage, thereby inducing reforming of the excess methane to carbon monoxide and hydrogen, which is an endothermic reaction. However, it is now common practice to reduce the oxygen levels in the tail gas to a minimum, by carefully controlling the airflow in the bleaching tower, such that only one pass is required over the catalyst.

The hot gas leaving the system, at a temperature up to 750 ºC can be used to generate steam and/ or power via a gas turbine (see **Figure 2.9**). One disadvantage of extensive integration, particularly with hydrogen-based NSCR, is that loss of hydrogen results in immediate loss of abatement. The nitric acid plant therefore needs to be shut down until hydrogen is restored.

The composition and form of the catalyst used for the above reactions have an important bearing on the flexibility of the operation, the degree of abatement achieved, the efficiency of fuel combustion and the catalyst life.

The advantages of using ceramic honeycomb supports for platinum-group metal catalysts for NO_X removal may be summarised as a compact process design, high activity, low pressure drop and good catalyst life. These advantages have led to honeycomb-based systems becoming widely accepted in preference to pelleted or metal ribbon support systems.

The activity of the catalyst is particularly important when methane is used as the reducing fuel because the methane molecule has high stability and is difficult to oxidise. Platinum has high stability coupled with good activity and also under reducing conditions it does not cause carbon formation, which may occur with palladium-based systems.

NSCR catalysts need replacement every two to three years.

The disadvantages of using a hydrocarbon as opposed to hydrogen as the reducing agent is that the treated tail gas can contain quantities of carbon monoxide (up to 1250 mg/ m^3) as well as unreacted and partially converted hydrocarbon.

2.1.3.3.6 Selective catalytic reduction with ammonia

In the case of the selective catalytic reduction (SCR) process the reducing agent, ammonia, reacts with nitrogen oxides to form nitrogen and water.

Unlike the non-selective processes, the reaction of the oxygen in the tail gas with the reducing agent is only of minor importance as only small amounts of the ammonia are oxidised this way.

Dependent upon the ratio of NO to NO_2, the ammonia reduces them to nitrogen by a mixture of the three reactions, all of which are strongly exothermic:

$4\,NO + 4\,NH_3 + O_2$ --------> $4\,N_2 + 6\,H_2O$

$NO + NO_2 + 2\,NH_3$ ----------> $2\,N_2 + 3\,H_2O$

$6\,N0_2 + 8\,NH_3$ -----------> $7\,N_2 + 12\,H_2O$

There are also small quantities of ammonium nitrate and nitrite formed by the reaction of the ammonia and nitrogen oxides. Catalysts commonly used are vanadium pentoxide, platinum, iron/ chromium oxide mixtures or zeolites.

The inlet temperature of the tail gas in the selective catalytic reduction depends on the catalyst used but is generally above 250 ºC

Process description

An outline of the SCR flowsheet is given as **Figure 2.11**

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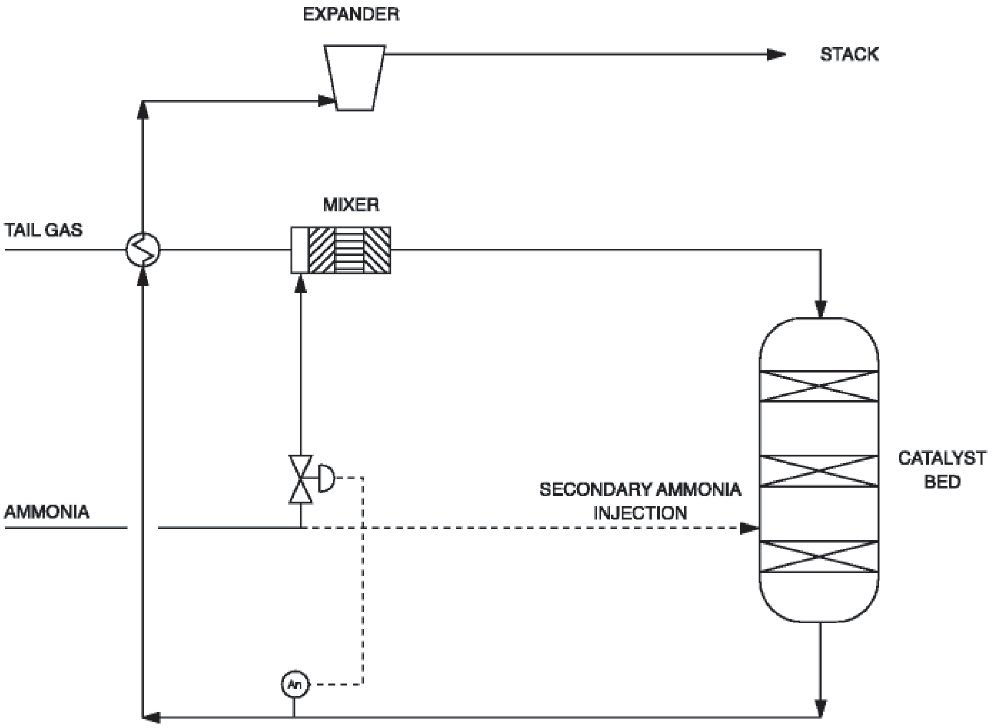


Figure 2.11: Outline of SCR flowsheet

The tail gas from the absorption tower is brought to the desired temperature through one or more heat exchangers. Ammonia is injected in the tail gas at the inlet of a mixer, which ensures homogeneous mixing of the two streams. The mixture then passes through the catalytic bed where the chemical reactions take place. These reactions being exothermic cause an increase in temperature.

The efficiency of the conversion of the NO_X gases can be in excess of 95%. Theoretically no excess ammonia is required, but in practice, due to ammonia slippage through the catalyst, some excess ammonia may be required and thus may give a release level of up to 10 mg/ m^3 from the plant stack.

The ammonia addition can be controlled to match a varying inlet NO_X concentration to ensure that the required outlet concentration of NO_X can be consistently achieved. It is evident that the use of this abatement process involves increased ammonia consumption. However, for plants with small capacities (say, less than 100 tonnes/ day of acid), with medium-pressure absorption and a NO_X content of 1200 mg/ m^3, as NO_2, in the tail gas, the process can be economically attractive compared to a high-pressure absorption plant designed to achieve the same low release limit for NO_X.

2.1.3.3.7 Comparison of nitric acid plant abatement systems

Conditions selected by the operator should be demonstrated to be the best practicable for optimum abatement of NO_X. Both catalytic reduction techniques and extended absorption are capable of achieving 200 mg/ m^3 NO_X for new plant.

Dinitrogen monoxide (nitrous oxide or N_2O) is produced in the catalytic ammonia oxidation reactor and, having passed through the absorption tower unaffected, is released from the plant exit stack. Its concentration is likely to be a function of conditions in the ammonia oxidation reactor, such as temperature, pressure and catalyst condition. Caustic absorption, extended absorption and catalytic reduction by ammonia will have little or no effect on the N_2O level but non-selective catalytic reduction by hydrogen or hydrocarbons can significantly reduce it.

For retrofitting of abatement equipment to existing nitric acid plants where the tail-gas NO_X concentration is in the range 600-3000 mg/ m^3, as NO_2, caustic absorption is unlikely to be a satisfactory option, even when beneficial use can be made of the sodium nitrite/ nitrate produced. There is also an associated operational problem since sodium nitrate has a tendency to freeze during the winter months.

Both SCR and NSCR techniques require the tail-gas to be at a pressure in excess of 4 barg and at a temperature at which the catalyst will operate - ie >250 ºC for ammonia and hydrogen, >500 ºC for methane and >400 ºC for other hydrocarbons -though SCR techniques using ammonia usually have a lower energy input requirement than NSCR techniques.

Where retrofitting of catalytic reduction equipment between the tail-gas reheaters after the absorber and the tail-gas expander is possible, the advantages of the ammonia (ie SCR) technique are:

- ammonia is always available on a nitric acid plant;
- very low NO_X concentrations can be achieved with an ammonia excess of less than 5% over the stoichiometric requirement of NO_X removal;
- no carbon monoxide or hydrocarbons are released to atmosphere and releases of ammonia are normally extremely small;
- oxygen in the tail-gas is only reduced after the majority of NO_X has been removed;
- there is a negligible increase in tail gas temperature, which is beneficial for materials of construction; and
- SCR systems are low-pressure-drop units that are capable of being retrofitted without sacrificing power recovery or affecting the balance of the plant energy network.

The disadvantages of SCR with ammonia are:

- ammonia 'slip' through the catalyst bed is possible and this can lead to a small ammonia release to atmosphere, although the latest catalyst technology has reduced this to a minimum;
- there is no reduction in N_2O concentration;
- tail-gas temperature after the expander must be kept above 1000 ºC to prevent condensation of ammonium nitrite and nitrate, which may have formed from the free ammonia present;
- catalytic reduction of NO_X can only start when the temperature is above 200 ºC, and this only occurs when the main plant is approaching stable operation; and
- the system can only start when temperatures are stable.

The advantages of NSCR relative to SCR are:

- N_2O is removed almost as effectively as NO_X;
- the reducing agent is likely to be relatively inexpensive in comparison to ammonia; and
- if a process upset occurs that causes insufficient reducing agent to be fed to the catalytic reactor, the NO_2 in the tail-gas is reduced in preference to NO and the emission remains colourless.

The disadvantages of NSCR relative to SCR are:

- unless hydrogen is used the tail-gas from the absorber has to be preheated to a higher temperature;
- the abatement system can only be started-up after the ammonia oxidation and NO_X absorption sections have stabilised and oxygen in the gas passing to the NSCR section is less than 3% - otherwise the temperature rise across the catalyst will be too high;

- unless hydrogen is used, significant concentrations of carbon monoxide (up to 1250 mg/m^3) and hydrocarbons are released in the tail-gas.;
- hydrogen, if provided from a refinery unit, is less reliable and may result in more frequent shut-downs; and
- the system is not available as an add-on system because of the need for a high-temperature gas expander.

2.1.3.3.8 Nitric acid plant start-up and transitional conditions

The required NO_X emission levels can be achieved with modern dual pressure nitric acid plants operating with an absorber pressure of approximately 11 barg; however, on start-up this pressure takes time to establish.

It can take up to an hour to establish stable operating conditions after process air compressor start-up although not at rated capacity, which may take several hours. Even on the best performing plants transient releases up to 1000 mg/ m^3 may be experienced.

Ammonia oxidation

During the 'light-up' of the catalyst care must be taken to ensure that there is even heat distribution across the face of the catalyst gauze so that the combustion reaction 'strikes' properly when ammonia gas is fed to the reactor. There are thermocouples provided to monitor the temperatures at various points immediately under the gauze. If correct operating conditions are not achieved within a reasonable period then there is a plant trip. The operators, who will be closely viewing the gauze during the start-up period, can also abort the start-up if their observations indicate a delay in establishing the correct ammonia combustion conditions.

A weak acid solution is produced in the cooler-condenser downstream of the reactor. However, on some plants, the quantity produced in the first 10-20 minutes after 'light-up' of the catalyst is put to drain as there is a chance that it could contain ammonium nitrite as a result of unreacted ammonia slipping past the catalyst gauze. A litmus test is sometimes carried out to ensure that acidic conditions have been established.

The acid product is also analysed to ensure that there is no continued operation with ongoing ammonium nitrate formation and the risk of detonation.

Catalytic abatement systems

Both catalytic NSCR and SCR abatement systems only become effective when the correct operating temperature has been reached and hence are not normally in operation during plant start-up or shut-down.

The heating of the tail - gas to the correct operating temperature for the catalytic abatement systems is normally achieved by exchanging heat with the gas leaving the ammonia oxidation reactor. With the thermal inertia of the absorber plant to be overcome and start-up rates being only 70% of normal operational rates, it can take up to an hour to establish effective NO_X abatement.

For non-selective catalytic systems on plant start-up, fuel cannot be introduced to the abatement system until the oxygen content has dropped from the initial 20% to about 2%, otherwise there will be overheating of the catalytic abatement unit. The 2% oxygen then has to be reacted before the nitrogen oxides can be reduced to nitrogen.

Nitric acid systems often have highly integrated energy systems as mentioned previously and shown in Figure 2.9. This would make the retrofitting of units with NSCR difficult. Not only would it require a change to the energy balance across the whole unit, but often the compressors, expanders and motors are located on one drive shaft in a 'train' configuration such that any changes would mean reconfiguring the train.

2.1.3.3.9 Best available techniques for Nitric acid plants

New large nitric acid plants can be designed to operate under steady conditions with a tail-gas concentration of less than 200 mg/ m^3, as NO_2, utilising extended absorption at high pressure with refrigeration followed by SCR treatment of the tail-gas. These levels may be achievable by absorption alone but they require optimal tower design, operation at a pressure of 11 barg or above and top tower temperatures below 15 ºC

Depending on the comparative environmental impact of N_2O and NO_X, the use of NSCR may be justified. BAT for existing plant would include retrofitting plants that do not include tail-gas abatement with a suitable system such that emissions are reduced to less than 300 mg/ m^3. The use of caustic scrubbing to produce co-product sodium nitrite may also be BAT and can achieve a level of 200 mg/ m^3.

2.1.4 Halogens and Hydrogen halides

2.1.4.1 Fluorine manufacture

2.1.4.1.1 General

Fluorine can be produced by the electrolysis of anhydrous hydrogen fluoride, dissolved in potassium bifluoride. The mixture has a melting point of approximately 80 ºC and the electrolytic cells are operated in the 85 - 90 ºC temperature range. Operation at these conditions is optimum and processing advantages include:
- low HF vapour pressure;
- use of tempered water as coolant;
- less corrosion at the anode; and
- accommodation of wider variations in electrolyte composition.

The principal reactions are:

$2\ HF \text{ --------->} F_2 + H_2$

$2\ KHF_2 \text{ ---------->} 2\ KF + F_2 + H_2$

Cells are individually connected to an extraction system. Hydrogen released at the cathode is scrubbed to remove traces of fluorine and hydrogen fluoride before release to atmosphere. Potassium hydroxide is preferred as the scrubbing medium since the solubility of potassium fluoride is greater than that of its sodium analogue. This reduces the risk of scrubber blockages.

Fluorine is produced under a slight positive pressure (50 mm water gauge). Nitrogen, introduced via sealing glands, serves both as a padding medium and as a carrier gas. The gas mixture is often fed directly to the user process. In circumstances involving the bottling of the nitrogen/ fluorine mixture, the gas is fed direct from dedicated cells to a compressor. No inventory of pure gaseous fluorine is maintained.

HF is recovered from the gas stream by condensation and recycled to the cells.

Releases to atmosphere from the process, into which the fluorine production is fed, are similarly scrubbed with aqueous potassium hydroxide.

2.1.4.1.2 Potential release routes

Releases to air

- Fluorine, hydrogen fluoride and hydrogen from absorbers.

Releases to water

- Potassium fluoride in scrubber liquors.
- Hydrofluoric acid, as a dilute solution following use of the emergency hydrogen fluoride scrubbing system.

Releases to land

- Redundant cell linings and carbon anodes.
- Waste electrolyte solids.
- Hydrogen fluoride absorbed on polyacrylamide or similar absorbent arising from emergency treatment of small spillages.
- Calcium fluoride from aqueous waste treatment to remove fluoride.

2.1.4.2 Chlorine and sodium/potassium hydroxide manufacture

All aspects of chlorine and alkali production are covered in the BREF for the Chlor-Alkali Industry, published in December 2001 (**Ref 1**), and it should be consulted for details of the processes and the BAT options for differing situations. The following is a more general overview.

2.1.4.2.1 General

Chlorine is principally produced by the electrolysis of sodium chloride brine. It is also produced from potassium chloride brine where potassium hydroxide is the required co-product, and as a by-product in the electrolysis of fused chloride salts producing sodium, magnesium, potassium or lithium. The basic process for the electrolysis of sodium chloride brine is shown in **Figure 2.12**.

2.1.4.2.2 Purification of brine

Brine from salt cavities at about 25% sodium chloride is purified by pH adjustment, precipitation, flocculation and settling of calcium, magnesium and iron impurities. Acidification of brine feed liberates CO_2 from brine-feed tanks, which may be vented to atmosphere. The quantity of solids for disposal depends on the purity of the rock salt used to make the brine. The sludge generated may be filtered, and the solid disposed of as cake to a licensed waste disposal facility.

Feed brine may also be produced in a resaturation process where pure crystalline salt is added in controlled quantities to recycled cell-room brine. Purification by pH adjustment, precipitation, flocculation and filtration is required, on a full flow or side stream basis, to keep levels of impurities at the required concentration. Membrane and mercury cells may use recycled brine requiring dechlorination by acidification, vacuum stripping and air blowing.

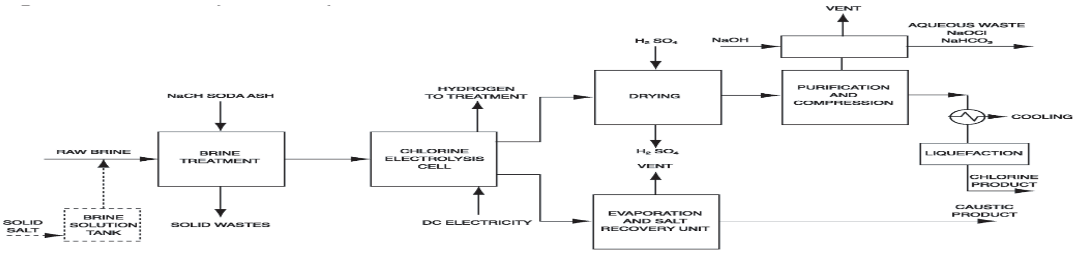


Figure 2.12: Basic chlorine production process

Sodium carbonate is generally used for precipitating calcium ions (as calcium carbonate) from the brine. CO_2 may also be used, with the advantage of reduced solids waste.

Brine purification for membrane cells is of critical importance to long membrane life and high efficiency. Impurities need to be removed down to parts per billion levels by ion exchange resin units, which then require regeneration with caustic soda and acid washing.

2.1.4.2.3 Electrolysis of brine

An aqueous solution of sodium chloride is decomposed electrolytically by direct current, producing chlorine, hydrogen and sodium hydroxide solution. This takes place in two parts: chlorine is evolved at the anode, and at the cathode caustic soda and hydrogen are produced directly or indirectly depending on the type of cell. A typical operation would involve large numbers of cells.

The overall reaction involved is:

$2\ NaCl + 2\ H_2O \text{ ---------> } Cl_2 + H_2 + 2\ NaOH$

There are three basic processes using different types of cells described in the following sections:

- the diaphragm cell process;
- the mercury cell process; and
- the membrane cell process.

(a) Diaphragm cell

Figure 2.13 provides an illustration of the basic cell. The anode area is physically separated from the cathode area by a permeable asbestos-based diaphragm. Saturated brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment.

Chlorine is generated at the anode whereas sodium ions migrate preferentially to the cathode where hydrogen is evolved and sodium hydroxide formed. Some migration of sodium ions across the diaphragm occurs in both directions and, as a result, current efficiency will be less than 100% and impurities such as sodium salts arise in the brine/caustic streams.

Caustic brine from the cells is separated into sodium hydroxide and salt in an evaporation unit. The sodium hydroxide produced contains residual sodium chloride. The salt separated is partly or wholly recycled to reconcentrate the incoming brine. Chlorine, with carbon dioxide, oxygen, and hydrogen impurities; is liquefied and tail-gas containing the residual chlorine, plus inerts, may be routed via sodium hydroxide absorbers to make sodium hypochlorite solution.

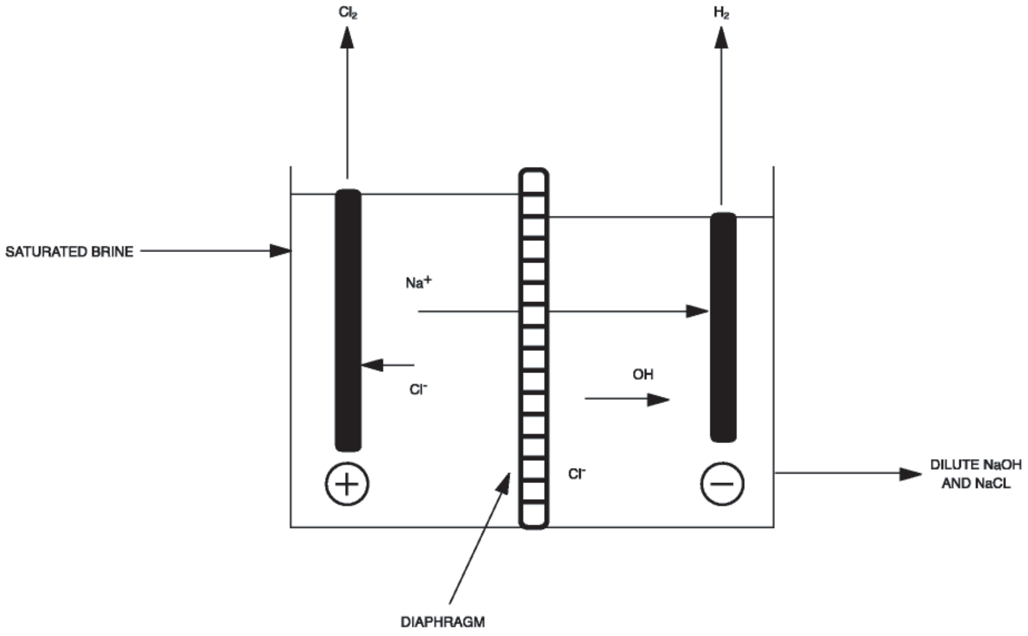


Figure 2.13: Simplified diaphragm cell

A special waste problem of the diaphragm process arises from the use of asbestos for the diaphragm. Asbestos waste is subject to the Asbestos Regulations and requires specialised handling and landfill requirements.)

(b) Mercury cell

An arrangement for the mercury cell is given in **Table 2.14**. In this process, mercury flows down the inclined base of the cell, forming the cathode. The hot saturated brine flows co-currently on top of the mercury and anodes are suspended in the flowing brine. Mercury cell technology is well established but, due to environmental concerns relating primarily to releases of mercury, intergovernmental pressure favours replacement of the mercury cell by other cell types.

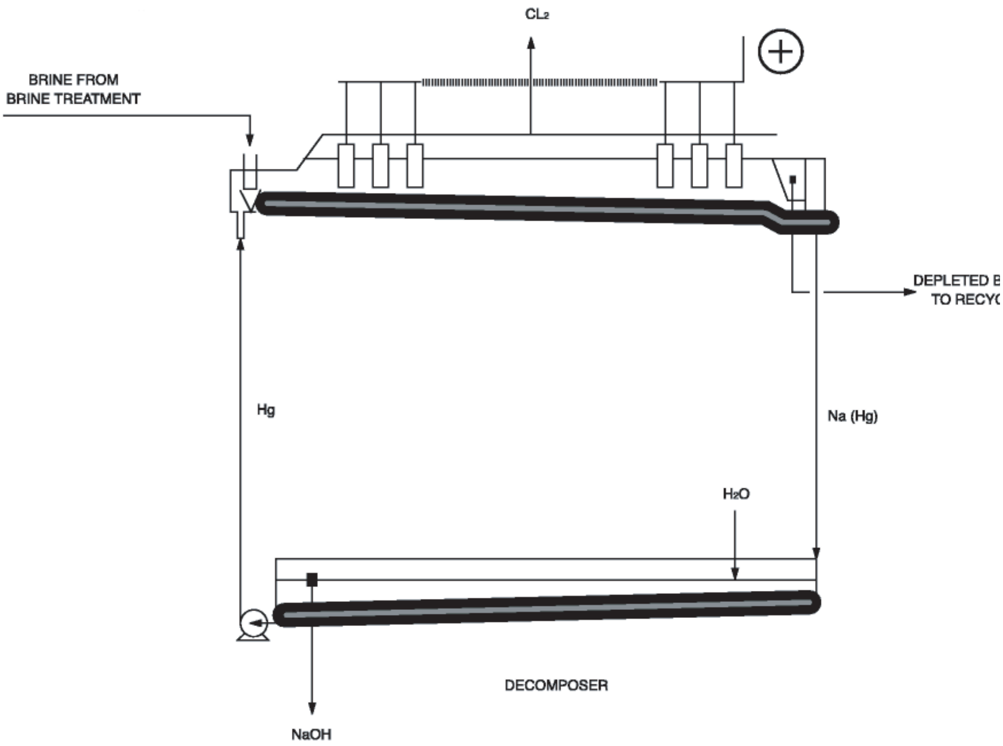


Figure 2.14: Mercury cell

Application of effective abatement techniques on existing mercury cell processes has led to substantial reductions in mercury emissions. These can effectively be considered as BAT for mercury cells and include the following:

- Removal of Hg from weak and strong hydrogen streams, by a combination of chilling, cooling and use of activated carbon.
- Combination of mechanical/ physical treatment to recover metallic mercury, downstream of the cells (eg vibration, vacuum cleaning, freezing, water jet treatment).
- Demercurisation of caustic soda, or potash, with plate or candle filters that have been pre-coated with activated carbon.
- Chemical treatment of process gases with oxidants such as 'hypo', chlorinated brine, H_2O_2 solutions
- Demercurisation of liquid effluents using sulphurous precipitation (to HgS), or specific ion - exchange resins.
- Distillation of mercury from solid wastes and recycle.
- Changes of cell configuration, such as steeper bases to reduce depth of mercury film, and vertical decomposers to minimise surface area of mercury. These changes assist in reducing the quantity of mercury required and its vaporisation.

The cost of changing from mercury cell technology to mercury-free technology is high, not just in plant hardware, but in training operators and gaining operational experience. Operators are therefore expected to plan their transition to mercury-free technology in such a way that significant sums of capital on further end-of-pipe abatement equipment is not spent to gain short-term environmental improvements if in the medium term a mercury-free solution has been clearly identified and is achievable.

In operation, chlorine gas is produced at the anode and a mercury-sodium amalgam at the cathode. This amalgam flows out of the cell over a weir into a decomposer where it reacts with water generating hydrogen and sodium hydroxide solution, typically 47-50 wt%. The mercury, stripped of its sodium content is recirculated back to the cell. Depleted brine from the cells is dechlorinated and may be recirculated or disposed of after treatment to remove mercury.

Hot moist chlorine from the cells contains small amounts of mercuric chloride. This is removed almost completely in the cooling process and may be fed back to the brine with the condensate.

Caustic liquor may be filtered in candle filters or leaf filters to reduce the mercury content to about 40mg/1.

The caustic produced from the mercury cell process has a small but measurable concentration of mercury. This can cause downstream contamination of the products manufactured by its use. In some cases, it has resulted in a measurable mercury discharge from processes using caustic soda produced from this process or its products. This can lead to effluent treatment problems. Much of UK industry uses the high-quality caustic produced from mercury cells. A change to production of chlorine/ caustic by other means may cause downstream operational problems due to differences in quality such as contamination of caustic with sodium chloride.

All contaminated materials that have come into contact with mercury (equipment, auxiliary chemicals, wash water, waste gases, scrap cells, etc.) should have the mercury removed prior to disposal.

(c) Membrane cell

A typical membrane cell is shown in **Figure 2.15**. Membrane cells are assembled on the same principle as filter presses/ plate heat exchangers in layers of membranes separated by spacers. The cells are therefore very compact and offer significant reductions in cell room area.

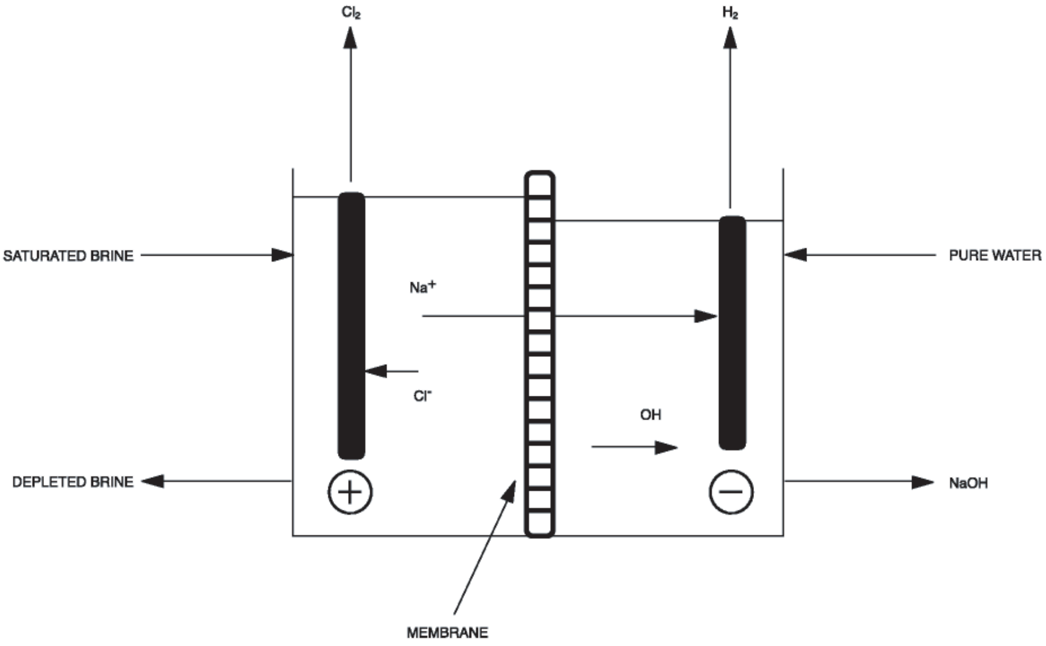


Figure 2.15: Simplified membrane cell

In the membrane cell process, the anode and cathode are separated by a cation-permeable ion exchange membrane. Only cations and water pass through the membrane. A demineralised water feed is required to the catholyte, which is recycled to the electrolyser compartment.

As in the mercury cell process, the depleted brine from the cells may be dechlorinated and recirculated using solid salt to resaturate the brine. In certain mercury cell plants a once-through brine flow is economic. However, this may not be attractive for some membrane cells due to cost, since the life of the membrane is dependent on very high-purity brine that has been treated by ion exchange. The 30-35% sodium hydroxide solution leaving the cell contains less than 260 mg/ m^3 salt, and concentration to 47-50% sodium hydroxide may be required for sale.

Chlorine product from the membrane process tends to be more aggressive chemically than chlorine produced by other cell processes, although the reasons are not completely understood. Consequently pipework and other materials will have shorter lives.

2.1.4.2.4 Advantages/disadvantages of cell types

Diaphragm cells

These must be operated near their specified capacity to allow successful operation. A mixed stream of caustic soda in brine is produced, which requires further treatment to produce caustic of the required strength and chloride content. Even after this treatment, the residual brine content may prevent its use in some applications.

The asbestos diaphragm does degrade with operation and the resultant asbestos waste requires specialised handling

Mercury cells

Chlor-alkali processes using mercury technology have an inherent disadvantage owing to products and by-products contaminated with mercury being released into the environment. BAT techniques, as described can reduce total mercury losses to about 1 g/ tonne of chlorine capacity but cannot completely prevent mercury from being released to the environment.

Cell room ventilation air can be a relatively large source of release of mercury to the environment.

Mercury removal is not normally attempted from ventilation air, as the concentrations are kept below 0.05 mg/ m^3 by ventilation, and treatment of the very large volumes of air involved would be very expensive. Mercury loss to cell room should be minimised by effective containment, including use of effective operating and maintenance techniques to minimise losses to the cell room.

Mercury in process air, eg from cell end-box ventilation, or the vacuum cleaning systems, can be treated by methods similar to those used for hydrogen.

Liquid effluents will also contain mercury, which will require treatment prior to discharge.

Mercury cell operations and their routine replacement produce quantities of solid wastes, which must be regarded as mercury-contaminated. Each cell requires replacement every six years or so. Periodically the cell is drained and the bare cell is rinsed with hydrogen peroxide to remove, as Hg2+, mercury that has amalgamated with the steel base-plate. Depending on the process, the total mercury lost as solids can be up to 24 g/ tonne chlorine production. Mercury-contaminated solid wastes are landfilled.

Caustic soda, chlorine and hydrogen produced using technology such as the membrane cell or diaphragm cell have the advantage of being mercury free.

Membrane cells

Membrane cells produce high-purity low-strength caustic soda. Their main problem is that very pure brine is required and the chlorine generated in the cell can be contaminated with 2-3% oxygen. Special corrosion-resistant construction materials are required in the initial higher-temperature zones of the plant.

This process has lower power usage, and has no mercury-containing product streams.

The advantages and disadvantages of the three cell types are summarised in **Table 2.2**.

Table 2.2: Comparison of Electrolytic Cells

	Advantages	Disadvantages
Diaphragm Cells	No mercury in products or wastes.	Poor performance during turn-down operation. Mixed product of dilute NaOH and brine requires further treatment and concentration, with significant energy use. Asbestos waste.
Mercury Cells	Proven and well known technology. Insensitive to production upset conditions. Lower investment at higher current densities (CDs). Capacity increase at most existing plants by CD increase. No NaOH concentration required.	Products and wastes contain mercury. Higher energy use. Higher cell maintenance,
Membrane Cells	Produce high-purity, low-strength NaOH. Reduced energy use. No mercury in products or wastes. More modern technology. Less maintenance. Easier operations.	Requires very pure brine feedstock. Higher investment. More sensitive to production upset conditions. NaOH needs concentration, increasing energy use. Need for higher level of plant personnel. Chlorine product can be contaminated with 2-3% 0_2. Special materials of construction required.

2.1.4.2.5 Chlorine gas treatment

Wet gas from the cells must be cooled, dried, compressed and liquefied under pressure by refrigeration. Export as chlorine gas (with impurities such as oxygen and hydrogen) to consuming plants elsewhere on the same manufacturing site, has benefits in minimising production of sodium hypochlorite in the final chlorine absorption plant.

(a) Cooling and drying

The drying of chlorine is accomplished by initial cooling of the gas from the cell. Excessive cooling should be avoided to preclude the production of chlorine hydrate. Sulphuric acid (96-98 wt%) is then used to reduce the moisture content to less than 130 mg/ m^3 in a series of contact towers. Waste acid is dechlorinated by air blowing and is normally sold, but may be reconcentrated for re-use or used for treatment of effluent. Chlorine produced from the sodium process receives similar treatment. However, owing to the presence of dust and fume the gas stream is first washed with a recirculating chilled water system comprising a spray tower followed by a packed tower. Solids in suspension are dealt with in an effluent treatment plant by pH correction and settling to remove suspended solids.

(b) Compression, liquefaction and storage

Efficient centrifugal machines can achieve multi-stage compression up to approximately 3.0 barg Compressor seals are fitted with a pressurised purge to inhibit leakage of chlorine to the atmosphere.

Automatic control of the compressor by-pass is used to maintain the cell's design pressure condition, which, under upset conditions, is also effected by relief to the chlorine absorption system in conjunction with a fan.

Chlorine liquefaction is undertaken in condensers, which are arranged to allow liquid chlorine to flow to stock under gravity. The chlorine contains hydrogen, oxygen, nitrogen and carbon dioxide contaminants. These must be allowed for in the subsequent use of the gas as a process feedstock, or in avoiding explosive concentrations during liquefaction of the chlorine. (Not all plants avoid explosive regimes. Some are designed to operate within these conditions, with vessels that are strong enough to withstand detonation.)

All liquid reliefs from chlorine storage tanks pass to closed expansion tanks and only thence by controlled release to the chlorine absorption plant. Refrigerated storage may be used as appropriate. The liquid chlorine from the bulk tank can be used as a feedstock for on-site processes, loaded into containers, road or rail tankers.

The selection of refrigerant to chill and liquefy chlorine gas has significant environmental implications. Refrigerants with significant ozone depletion potential such as chlorofluorocarbons (CFCs) should be replaced with non-ozone depleting refrigerants. 'Transition' refrigerants such as hydrochlorofluorocarbons (HCFCs) should also be replaced in the longer term. Refrigerants that are removed must be sent to an authorised operator for destruction.

Conversion of existing systems will involve consideration of several factors, such as:

- review of thermo-physical properties;
- compatibility with compressor lubricants;
- heat transfer efficiency;
- power requirements; and
- health and safety.

(c) Distillation

Chlorine is sometimes distilled to remove contaminants. Amongst these can be nitrogen trichloride, and highly chlorinated materials such as hexachloroethane, hexachlorobenzene and hexachlorobutadiene arising from traces of organic materials in the brine feedstock. These chlorinated heavies tend to be fully substituted and should be destroyed by thermal oxidation with recovery of hydrogen chloride

2.1.4.2.6 Hydrogen gas treatment

(a) Strong hydrogen

Hydrogen produced from the amalgam 'decomposer' is referred to as 'strong hydrogen', indicating its high concentration. It is formed from the exothermic reaction of sodium amalgam with water. Mercury vapour is entrained in the process stream. Cooling the gas stream reduces the concentration of mercury to a few mg/ m^3. Mercury vapour condenses and is collected. It is reported that lower levels can be achieved using more advanced adsorbents such as molecular sieves in combination with cooling methods to attain emission levels equivalent to 2.5 mg Hg/ tonne chlorine.

Hydrogen may be compressed and cooled, to reduce the mercury content further. Additional purification can be achieved using activated carbon adsorbers. The hydrogen is either used as a feedstock to other manufacturing processes such as HCl manufacture, stored prior to being sold, burned as a fuel, or less probably vented to atmosphere.

A two-stage method for the removal of mercury from hydrogen currently in use in Europe appears to be particularly effective.

The first stage of the process involves compressing and cooling the hydrogen to -20 ºC These conditions generate ice crystals, which nucleate the gas, promoting removal of the mercury. This is reported to reduce the mercury content to less than 1 ppb in the exit gas, which is then fed into the second stage.

The second stage passes the hydrogen over palladium, which amalgamates with the traces of mercury remaining, completing the removal process.

(b) Weak hydrogen

A further hydrogen stream is produced from mercury cells during the wash operations performed on the mercury, on its entrance to, and exit from, the cell. The quantities of hydrogen are much smaller, and are diluted with air to maintain the concentrations below explosive limits. This hydrogen stream also contains mercury, which may be treated by addition of chlorine. The chlorine reacts with mercury to form Hg_2Cl_2, which deposits as a solid. The cleaned gas is vented to atmosphere.

The mercurous chloride residue is washed with chlorinated brine, which reacts to form $HgCl_4^{2-}$ and is recycled to the electrolysis plant. During electrolysis the $HgCl_4^{2-}$ complex produces mercury metal and chlorine.

2.1.4.2.7 Potential release routes

Releases to air

- Chlorine from absorbers.
- Carbon dioxide may be vented from brine acidification tanks.
- In the mercury cell process, mercury may be released in vapours from brine systems, process air and cell room ventilation system.
- Fugitive emissions from chlorine handling systems.

Releases to water

- Waste brine from the cells. Note:- Brine is purged from membrane cells to reduce the levels of sodium sulphate and/ or sodium chlorate in the cells.
- Chlorine-contaminated water containing residual dissolved free chlorine or hypochlorite.
- Spent sulphuric acid from chlorine drying is discharged, unless sent for re-use.
- Waste scrubber liquor (hypochlorite in caustic) from the absorption plant.
- Brine mud, filter washing and waste liquor from the brine purification plant.
- Mercury contamination may be present in any liquid effluent discharges from mercury plants.
- Mercury contamination of rain-water effluents from mercury process plants.

Releases to land

- Dewatered filter solids from brine purification.
- Bagged asbestos from scrap diaphragms.
- There is a risk of mercury discharge in all solid wastes from mercury plants, eg treatment sludges, spent ion exchange resins, spent active carbon from water treatment and scrap cells.
- Membranes from membrane cells.

2.1.4.2.8 Chlorine Production as a by-product

(a) Production of Sodium by electrolysis of fused sodium chloride

Chlorine gas is produced by sodium cells as a by-product in the electrolysis of fused sodium chloride mixed with calcium chloride and barium chloride. This is undertaken at 600 ºC in a brick-lined diaphragm cell with graphite anodes and a water-cooled steel cathode. The process is hot and dusty with many manual operations. The by-product chlorine is contaminated with salt and siliceous particles, which must be removed in an extra washing stage, but is otherwise treated as chlorine from brine cells.

(b) Production of Magnesium by electrolysis of fused chlorides

Chlorine gas is produced in the electrolysis of a fused salt mixture of magnesium chloride/ sodium chloride/ calcium chloride. The technology is similar to the process described for the production of sodium.

Chlorine produced by the above processes is subsequently handled as described earlier in this section, except that additional front-end clean-up is required.

2.1.4.3 Bromine manufacture

2.1.4.3.1 General

Bromine occurs in nature as soluble bromide salts. There are two chemically similar processes worldwide for extraction of bromine: a two-stage process from sea water and a simpler one-stage process from richer brines. Only the sea water process is used in the UK and that plant is facing closure.

By-product liquids containing bromine or hydrogen bromide may be either returned to the bromine plant from users, or treated with chlorine on- site, for the recovery of bromine.

2.1.4.3.2 Extraction from sea water

The sea-water process is illustrated in **Figure 2.16**.

Sea water under ambient conditions, containing about 65 mg/ litre of bromine as various bromides and bromates, is acidified with sulphuric acid to pH 3-3.5 to avoid the further formation of bromates. Chlorine is added to 5-10% excess over stoichiometry. This releases the bromides as free bromine, which is then stripped out by a large counter-current flow of air in a packed tower. The bromine-laden air is contaminated with chlorine. The reaction is:

$2\ NaBr + Cl_2$ ----------> $Br_2 + 2\ NaCl$

In the first recovery stage, bromine-laden air is fed to an absorber into which water is sprayed. Immediately prior to the water spray, sulphur dioxide is injected, which along with water reacts with the bromine to form hydrobromic acid and some hydrochloric acid. This tends to be in droplet form and the off-gas stream is therefore passed through a bed coalescer where disentrainment of the hydrobromic acid and hydrochloric acid occurs. The blown air is recycled.

The governing equation is:

$Br_2 + SO_2 + 2H_2O$ ------------> $2HBr + H_2SO_4$

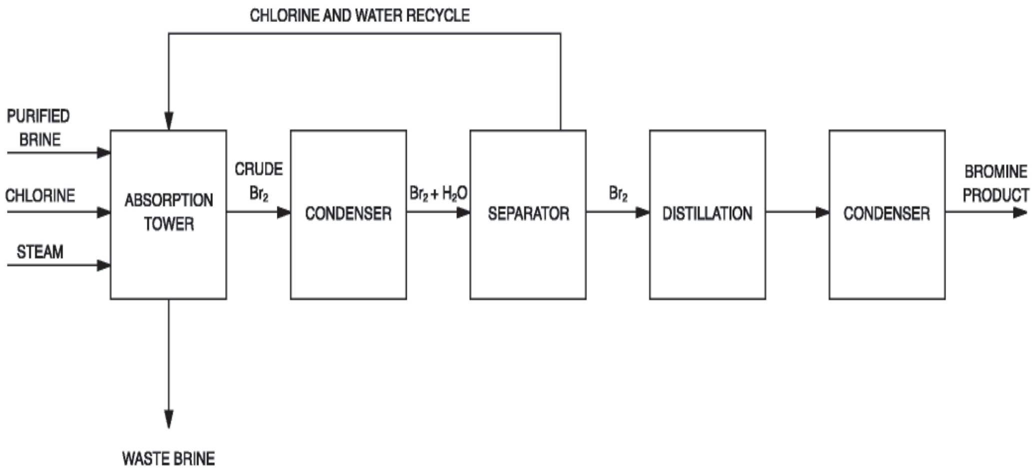


Figure 2.16: Bromine manufacture

The excess sulphur dioxide in the gas stream passes through the bed coalescer. This gas stream is then fed to the bottom of the bromine stripping column where it contacts the stripped brine containing residual (unstripped) free halogen. This reduces the level of free halogen typically to 18-20 mg/ m^3 in the discharged waste brine under normal operating conditions.

Mixed acids (mainly hydrobromic acid and sulphuric acid) are transferred from the coalescer to the bulk storage tanks to be used as feedstock for the next stage of the bromine recovery process.

In the second concentration stage, the bromine is recovered by re-chlorination of the acid liquor. Two variants of this are in current use.

The first method uses two packed columns. The mixed acid stream is contacted with chlorine (less than stoichiometry) added at ambient temperature in the first column. The bromine liberated forms a separate phase at the bottom of the column and is separated off to be combined with bromine formed in the second column.

The aqueous phase from the first column with dissolved bromine and hydrogen bromide is passed into a second column where further chlorine (to slight excess) is added together with steam at the bottom of the column.

The second column bottom temperature is controlled at 100 ºC so that the liquor leaving the base of the column, stripped of dissolved gases, is clear and colourless, containing only trace levels of chlorine or bromine. (This effluent liquor from the column is used to acidify incoming brine in the first part of the process). The overhead temperature is maintained at about 95 ºC and is at atmospheric pressure.

The second method uses one column. There is no pre-stage chlorination. All of the chlorine and steam is added at the base of the column, which is operated as described above.

The disadvantage of this second method is that a lower- quality aqueous effluent is generated with higher levels of free chlorine and bromine.

Overhead condensers produce a mixture of liquid bromine and water. This is separated under gravity into two phases, bromine and an acid liquor, which is recycled to the process.

Vents from the separators pass up a packed tower where they meet the incoming acid liquor and where they receive a primary scrub to remove bromine and chlorine before passing to the bromine scrubber.

The bromine scrubber uses sea water, which then passes to the dilute acid tank and is recycled. The effluent from the scrubber contains dissolved bromine and normally returns to the dilute acid tank. It is possible for this effluent to be put to drain in emergencies. It must not pass directly to an open drain.

The dilute acid tank has a sea water scrubber and a second caustic soda scrubbing stage for treating vented gases. The caustic scrubber effluent is rejected, at 4% caustic containing bromides, and recirculated into the dilute acid tank. Failure to replenish the caustic would allow the presence of dissolved free bromine.

Wet bromine, containing traces of chlorine, from the separators is contacted with the incoming hydrobromic/ hydrochloric acid feed to remove the chlorine.

After dechlorination some of the wet bromine is dried counter-currently with concentrated sulphuric acid prior to sale or use in the manufacture of hydrogen bromide. The rest of the bromine may be used in processes where wet bromine is acceptable.

The sulphuric acid waste stream saturated with bromine from the drying operation is recycled to acidify incoming sea-water.

2.1.4.3.3 Bromine loading and storage

Dry bromine is loaded into road or rail containers or bottles specifically designed for its transport. Stock tanks are fitted with double bursting discs with a tell-tale indicator between, venting to a lead-lined expansion tank, which is then able to vent to the bromine scrubber system.

Transfer is accomplished by compressed air from an automatic pressure-controlled system. All tanks are equipped with breathers leading to the vent scrubber via a non-return valve.

2.1.4.3.4 Potential release routes

Releases to air

- Bromine, chlorine and sulphur dioxide from absorbers and strippers.

Releases to water

- Sea water, depleted in bromides but containing the sulphuric acid used to acidify the brine, is returned to the sea at a location remote from the intake. There is likely to be a slight excess of mercury compared with natural levels in sea-water, if the stripping chlorine originates from the mercury cell process.

Releases to land

- Wastes from plant maintenance.
- Solids from brine treatment.

2.1.4.4 Iodine manufacture

2.1.4.4.1 General

No primary iodine manufacture or recovery is undertaken in the UK, although resublimation of crude iodine to produce a high-purity product is carried out. Iodine was formerly manufactured by the burning of seaweeds (kelp) but is now recovered from iodine-containing brines in the United States and from nitrate deposits in Chile. The Japanese are major producers.

2.1.4.4.2 Potential release routes

Iodine is unusual in having a significant vapour pressure (90.5 mm Hg) at its melting point of 113.6 ºC Hence usage and resublimation of iodine can give rise to atmospheric release of iodine vapour, and also iodine dust. Containment of this is discussed under potassium iodide production (see **Section 2.1.5.6**).

2.1.4.5 Hydrogen fluoride and hydrofluoric acid manufacture

Hydrogen fluoride in its anhydrous form exists as a low-boiling-point (19.5 ºC) colourless liquid. It is highly soluble in water, forming hydrofluoric acid, and fumes strongly in contact with moisture. The vapour is corrosive and highly toxic, and both the vapour and aqueous solutions can cause particularly serious burns to skin and tissue which warrant a specialist medical response.

2.1.4.5.1 Anhydrous HF production

Hydrogen fluoride is manufactured by the reaction of fluorspar (calcium fluoride) with concentrated sulphuric acid. For anhydrous HF (as opposed to hydrofluoric acid production) it is necessary to ensure elimination of water from the reaction mixture. This is achieved in two ways:

- pre-drying of calcium fluoride powder to remove residual traces of moisture (this can contain 5-10% moisture, as received), the drying operations possibly giving rise to dust emissions; and
- use of oleum to absorb excess moisture.

The reaction is normally carried out in sloping and heated (300 ºC) rotating kilns. The two raw materials are fed into one end of the rotary kiln and calcium sulphate removed from the other. Hydrogen fluoride gas, together with a number of gaseous and particulate impurities, is withdrawn under suction via a header at the inlet end of the kiln. An emergency gas removal system, ducted to a stand-by scrubber, is commonly installed on the outlet end.

The spent calcium sulphate from the reaction is deliberately discharged from the kiln still containing 1-2% calcium fluoride, since it is more free-flowing with this composition. This acidic by-product commonly generates sulphur trioxide fume. Emission of this fume is prevented by admixing with calcium oxide in the discharge conveyor system, which neutralises acidic components with no consequent release of sulphur trioxide to air.

Crude hydrogen fluoride gas, plus impurities, is drawn from the kiln under suction at circa 160-180 ºC, by tail gas fans at the end of the scrubbing/ condensing train. It is initially scrubbed and cooled with concentrated sulphuric acid to remove dust, sulphur trioxide mist and water vapour. The cooled, scrubbed gas mixture of hydrogen fluoride contaminated with sulphur dioxide and fluosilicic acid at about 20 ºC (only slightly above its boiling point) passed to condensers to produce a liquid containing 98% hydrogen fluoride.

Hydrogen fluoride of this purity is acceptable for some manufacturing operations such as aluminium fluoride, synthetic cryolite and sodium fluoride production.

Where the anhydrous hydrogen fluoride produced as above is not of acceptable quality for further manufacturing operations, it can be purified further by fractional distillation. Fractional distillation of the crude 98% material will yield 99.9% anhydrous hydrogen fluoride. Low-boiling-point substances such as sulphur dioxide, fluosilicic acid and silicon tetrafluoride, which leave the top condenser of the rectifying column, will be saturated with hydrogen fluoride. These are passed through a concentrated sulphuric acid absorption column to recover the hydrogen fluoride. This is subsequently released from the acid when it is used as the scrubbing medium in the pre-purifying stages.

The exit gases are further scrubbed in a water absorption scrubber, to yield an aqueous solution of fluosilicic acid. Tail gases from this unit are commonly vented to atmosphere via a further water absorption unit, through which fluorine-containing tail gases from other site operations are also channelled.

This will commonly include:

- scrubbed gases exiting from the kiln's emergency scrubbing system;
- gases from storage tank vapour spaces; and
- venting and purging occurring during tank filling and transfer operations.

Anhydrous hydrogen fluoride can be stored in mild steel pressure tanks. Tanks may be grouped within a sealed, and alarmed, secondary containment structure, with permanent connections from the tanks themselves, and the containment unit, to the site scrubbing systems.

The alarm is specific for the detection of hydrogen fluoride vapour.

Abatement of HF is generally through the water scrubbing systems as described above. These are very effective due to the high solubility of HF.

2.1.4.5.2 Hydrofluoric acid process

The production of hydrogen fluoride gas for the manufacture of hydrofluoric acid is similar to that for anhydrous hydrogen fluoride. The main differences are that the calcium fluoride feedstock need not be dried, and concentrated sulphuric acid may be used instead of oleum.

The strength of the concentrated sulphuric acid used, in conjunction with the moisture content of the calcium fluoride, dictates the initial concentration of acid obtained from the hydrogen fluoride condenser. An initial concentration of 70-80% is normally obtained.

Hydrofluoric acid fumes at concentrations above 40%, so the condenser is followed by a counter-current absorption tower train, typically of reinforced plastic construction. This allows preparation of acids of different commercial strengths in the range 40-70%. A separate final scrubber tower, not part of the counter-current train uses fresh water to minimise the release of hydrogen fluoride to air. Graphite heat exchangers may be used in areas of high corrosion risk.

Storage tanks for hydrofluoric acid are commonly of spirally wound polypropylene and filled by dip pipe to minimise splash and fuming. Ball blanketing is also used. Tanks breathe to atmosphere via a demister and water scrubber, the liquor of which is used for acid strength adjustment.

Abatement of hydrofluoric acid vapour is generally through the water scrubbing systems described for HF.

2.1.4.5.3 Potential release routes

Releases to air

- Particulates (losses from dust control equipment).
- Hydrogen fluoride from absorbers.

Releases to water

These will comprise combinations of:

- Dilute fluosilicic acid. Note:-The principal component as regards fluorine contribution will be fluosilicic acid. This arises as a by-product due to the presence of silica in the calcium fluoride raw material. Although some commercial outlets exist for fluosilicic acid, it is appropriate to use fluorspar with the lowest practicable silica content.
- Liquors from water-fed process and emergency scrubbers.
- Spent alkaline scrubbing liquors.

Releases to land

- Calcium sulphate. Note: Approximately 3.7 tonnes of waste calcium sulphate is generated per tonne of 100% hydrogen fluoride produced. This is neutralised with lime and has historically been disposed of to landfill. Increasingly, outlets are being sought for its incorporation in manufactured building products.
- Calcium fluoride precipitated from aqueous effluent.

2.1.4.6 Hydrogen chloride and hydrochloric acid manufacture

2.1.4.6.1 Anhydrous HCl production routes

Anhydrous hydrogen chloride is obtained principally from the following sources:

- as a by-product in the chlorination of hydrocarbons;
- as a by-product from the thermal cracking of chlorinated hydrocarbons;
- from the combustion of hydrogen and chlorine; and
- by evaporation of 36 wt% hydrochloric acid.

2.1.4.6.2 By-product hydrogen chloride

(a) Chlorination of hydrocarbons

Hydrogen chloride is produced as a by-product of chlorination substitution reactions.

(b) Thermal cracking of chlorinated organic compounds

As part of PVC/ vinyl chloride production, dichloroethane (DCE) is cracked to hydrogen chloride and vinyl chloride monomer (VCM) by passing through a heated tubulars reactor, followed by a DCE quench to stop the reaction selectively at the optimum VCM fraction. Hydrogen chloride is separated by distillation and refrigeration to produce anhydrous liquid hydrogen chloride for sale, or for use in oxychlorination reactors to make further DCE. These processes are described in more detail in IPPC Guidance Note S 4.01 ('**Ref 23**).

Abatement of HCl is generally through the water scrubbing systems as described above. These are very effective due to the high solubility of HCl.

2.1.4.6.3 Combustion of hydrogen and chlorine

This particular manufacturing operation is often carried out as an ancillary process to the manufacture of chlorine. There is thus the potential for carry-over of contaminants from the previous manufacturing operation, e.g. mercury. So-called synthetic hydrogen chloride is made by burning chlorine in an excess of up to 20% of hydrogen in proprietary carbon burners. A graphite bursting disc, relieving to stack in case of explosion, is provided.

In normal operation, hydrogen burning is initiated with air before chlorine is admitted. Inert non-condensibles pass to atmosphere via a scrubber and stack. The process is simple and automatic controls are effective. Very pure hydrogen chloride can be made, depending on the purity of the feed gases.

Extra high purity for use in pharmaceutical and semiconductor manufacture can be achieved by drying and distilling aqueous hydrogen chloride. Dry hydrogen chloride gas produced is compressed and liquefied under refrigeration.

2.1.4.6.4 Evaporation of 36 wt% hydrochloric acid

Aqueous HCl is preheated and fed to a falling film evaporator. The falling film evaporator is heated with steam and wet HCl gas is removed as overheads and condensed, then dried by direct contact with sulphuric acid. Depleted hydrochloric acid is treated with the 36% acid to produce a 28% solution. The 28% acid is available as an absorbent for any potential gaseous HCl releases.

Abatement of hydrochloric acid vapour is generally through the water scrubbing systems.

2.1.4.6.5 Hydrochloric acid production

Anhydrous hydrogen chloride (AHCl) is absorbed in water in a packed column constructed in corrosion-resistant material. The hydrogen chloride/ water equilibrium is complex, and the concentration of product hydrochloric acid is limited in practice to 36% by vapour pressure considerations.

2.1.4.6.6 Potential release routes

Releases to air

- Hydrogen chloride from absorbers.
- Excess hydrogen (in combustion of H_2 and Cl_2))
- VOCs from organic chlorinations

Releases to water

- Sodium chloride in spent absorber liquors.

Releases to land

- None.

2.1.4.7 Hydrogen bromide and hydrobromic acid manufacture

2.1.4.7.1 HBr production routes

Commercial anhydrous hydrogen bromide is obtained principally from three sources:

- from the combustion of bromine and hydrogen;
- from the catalysed reaction of bromine and hydrogen; and
- as a by-product from the bromination of hydrocarbons.

The first two are both followed by a second-stage catalytic reaction to achieve 100% conversion of the bromine.

2.1.4.7.2 Reaction between bromine and hydrogen

Anhydrous gas (AHBr) is produced industrially by burning bromine in the presence of excess hydrogen at 500 ºC or by reacting it with hydrogen over platinised silica gel at 375 ºC The second stage of the conversion is achieved in a catalytic reaction over activated carbon at 250 ºC

Hydrogen from high-pressure cylinders is reduced in pressure to 2 barg and steam-heated to 100 ºC Bromine, dried over concentrated sulphuric acid, is transferred from liquid stocks by padding nitrogen and is vaporised in a steam-heated monel vaporiser. Air must be excluded, since traces of oxygen will react with the hydrogen and the water will cause corrosion in downstream monel and stainless steel equipment.

A mixture of hydrogen (5% excess) and bromine gases is ignited by spark discharge in a stainless steel burner. A 99.9% conversion of bromine is possible at this stage, with the exit gas temperature of 400-410 ºC controlled by adjusting the cooling water supply. The gases then pass through heated pipes to the catalytic activated carbon reactor to complete the conversion of bromine to hydrogen bromide.

The exit gases (hydrogen bromide and a small amount of residual hydrogen) are then cooled and pass to plants using the AHBr or to absorbers to produce hydrobromic acid. Normal practice is to recover hydrogen bromide in aqueous scrubbers to produce hydrobromic acid in strengths up to 47 wt% - the binary azeotrope contains 47.5 wt% - with residual gases vented via a caustic scrubber.

Gaseous emissions from the plant are fed to a caustic scrubbing tower. Caustic is preferred for the exit vent scrubbing due to the reduced vapour pressure of the HBr in the vent gas, when compared with aqueous scrubbing

2.1.4.7.3 Hydrobromic acid production

Hydrogen bromide is very soluble in water, making an acid solution of hydrobromic acid. It can be manufactured as an ancillary process to anhydrous hydrogen bromide production by absorption in a water scrubber as described above.

Hydrobromic acid is also recovered from off-gas streams arising from organic bromination reactions using aqueous scrubbers. Dependent on its origin, hydrobromic acid may therefore contain traces of organic material.

2.1.4.7.4 Potential release routes

Releases to air

- Hydrogen bromide and bromine (or traces of organics) losses from absorbers.
- Excess hydrogen (for the bromine -hydrogen process)

Releases to water

- Sodium bromide and sodium hydroxide in spent absorber liquors.

Releases to land

- Spent catalyst.

2.1.5 Activities using or releasing Halogens or Hydrogen halides

2.1.5.1 Lithium manufacture

Lithium is produced by the electrolysis of a molten eutectic mixture of lithium chloride and potassium chloride in gas-fired cells. Chlorine gas, co-produced in the cell, is absorbed in sodium hydroxide to produce a sodium hypochlorite solution for commercial sale.

There are no membranes or separators within the cell to enforce separation of lithium and chlorine, avoidance of recombination being dependent on the induced draught extracting the chlorine gas. The gas streams are manifolded to a venturi, followed by a packed scrubbing column, where sodium hydroxide (15% initial concentration) is used to produce sodium hypochlorite solution.

Further information on sodium hypochlorite production is given in **Section 2.1.5.4**.

Lithium chloride is generally manufactured on a batch basis by the addition of lithium carbonate powder to concentrated hydrochloric acid (34%). Effervescence results, with the carbon dioxide given off carrying over some hydrochloric acid spray. The mixing tank is under slightly reduced pressure, resulting from the induced draught on the scrubber exhaust. Off-gases are scrubbed with dilute caustic soda in a single-stage glass-fibre reinforced plastic and PVC-lined packed scrubber. Crystallisation of lithium chloride is effected by evaporation or spray-drying.

Releases to air

- Chlorine and carbon dioxide from absorbers.

Releases to water

- Sodium chloride and residual sodium hydroxide in scrubber liquors.

Releases to land

- Spent eutectic (lithium and potassium chlorides contaminated with a build-up of impurities) requires periodic disposal to landfill.

2.1.5.2 Ferric chloride manufacture

Chlorine gas and hydrochloric acid are used in the batch manufacture of ferric chloride solution. Mild steel off-cuts are commonly used as the source of iron. Ferrous chloride (10%) solution is made using fresh or by-product hydrochloric acid, spent pickling liquors (containing 2-3% hydrochloric acid) and steel off-cuts. Ferrous chloride (25 wt%) is added. This mixture is then reacted with gaseous chlorine, in a lined and lidded vessel, to oxidise the ferrous chloride to ferric chloride. Additions are regulated to produce a 43-44% solution.

In the continuous process, the plant comprises an iron dissolver, a packed ferrous tower and a packed ferric tower. Pickle liquor and dry chlorine are fed counter-currently with the pickle liquor introduced into the ferrous tower and the chlorine into the ferric tower. The reaction vessels are exhausted to atmosphere via a scrubber, with 10% ferrous chloride liquor being used as the scrubbing medium.

Releases to air

- Chlorine and hydrogen chloride from absorbers and ferrous towers.

Releases to water

- None.

Releases to land

- Sludges accumulating in reaction vessels are periodically disposed of at a licensed landfill.

2.1.5.3 Aluminium chloride manufacture

Aluminium chloride is made in a continuous process from aluminium metal and chlorine. Ingot aluminium is charged to a refractory crucible furnace in which it is melted (660 ºC). Dry chlorine is passed into the molten charge and forms aluminium chloride vapour. This reaction is exothermic and sufficient to melt further aluminium as it is introduced. External indirect cooling is also required. The aluminium chloride vapour leaves the furnace through a vapour duct, which passes to air-cooled condensers. Aluminium chloride crystals form on the condenser walls and are periodically removed (by vibrating the walls of the vessel), crushed, screened and packaged in moisture-tight containers.

Packaging, product handling and storage conditions must avoid contact with moisture and may require dry air or nitrogen conditions.

With proper regulation of the chlorine addition rate, very little free chlorine should exist in the exit gases from the furnace. However, a protective scrubber, using caustic solution, is placed beyond the condenser to absorb any unreacted chlorine, hydrogen chloride and aluminium chloride that may pass through. The waste liquid effluent, containing hypochlorite from the scrubber, can be catalytically treated to make a brine solution.

Poly-aluminium chloride (PAC) is manufactured using a batch reaction in which hydrated alumina is reacted first with hydrochloric acid, then with sulphuric acid at elevated temperature in a two-stage process. The basic forms of aluminium sulphate and aluminium chloride are then reacted together for the final polymerisation stage. The product is cooled, filtered and diluted with demineralised water. The products are PAC and hydrated alumina, which is either recycled or disposed of as a controlled waste.

Releases to air

- Chlorine and hydrogen chloride from absorbers
- Particulate aluminium chloride dust from classifying and packaging.

Releases to water

- Caustic/ brine/ solution from catalytic treatment.

- Soluble aluminium compounds removed as hydroxides.

Releases to land

- Castable refractory (drosses and inert impurities in the aluminium feed material) removed from the furnace periodically during maintenance.
- Spent hydrated alumina from the PAC process.

2.1.5.4 Sodium hypochlorite manufacture

Sodium hypochlorite is commonly obtained as the tail gas scrubber liquor in chlorine production. A solution of caustic soda is circulated, generally through a packed scrubbing column.

It can also be obtained by selectively scrubbing tail gas from the chlorination of organic compounds using caustic solution.

An alternative method includes dedicated in situ electrolysis of high-purity brine using a proprietary membrane process. The chlorine is immediately reacted with a bleed of the co-product caustic soda to yield the hypochlorite. Hydrogen is normally vented to atmosphere.

In some instances, liquid chlorine may be vaporised and fed directly to a purpose-built scrubber. The reaction is very exothermic. Heat extraction by use of an exchanger in the circulation loop will be required at higher production rates. This also minimises sodium chlorate production.

The product must be maintained above pH 11, to minimise decomposition. Contact with transition metal compounds (Ni, Co, Cu, Fe) also catalyses decomposition (and these are used to decompose excess hypochlorite on occasions). Hence the materials used for plant and equipment are commonly high-performance plastics or rubber-lined steel.

Abatement

The abatement techniques are typically those of chlorine abatement processes. They include scrubbing of off-gases to remove chlorine and treatment of liquid wastes from the electrolytic process with sodium thiosulphate to minimise free chlorine. Acidic liquid wastes are segregated and neutralised before thiosulphate treatment. The combined wastes are discharged as aqueous waste.

Releases to air

- Chlorine from absorbers.
- Hydrogen from electrolytic process.

Releases to water

- The in situ electrolytic process produces a neutralised aqueous waste.

Releases to land

- None.

2.1.5.5 Phosgene (carbonyl chloride) manufacture

The significant processes using phosgene in the UK are predominantly for organic chemicals manufacture. Liquid phosgene may be manufactured for sale.

Phosgene is manufactured from gaseous chlorine and carbon monoxide. In most cases gaseous phosgene is required for various downstream processes. Phosgene is supplied directly as crude, where there is no need for purification such as in the production of isocyanates, or alternatively as pure phosgene as in the production of polycarbonates. The specific plant design concept depends on required product purity, its intended use and raw material specification as well as on local conditions and regulations.

Typically, phosgene plants for production of gaseous phosgene have a capacity of between 20 and 600 kg/ hr of phosgene and consist of two main process units: reactor and absorber. Carbon monoxide can be supplied in gas cylinders or can be generated in situ by partial combustion of liquified petroleum gas (LPG), coke, natural gas, etc. Chlorine is usually supplied as a liquid in cylinders or from bulk storage located on-site.

Phosgene is manufactured by the exothermic gas-phase catalytic reaction of chlorine and carbon monoxide at temperatures of 150-180 ºC and pressure typically 1.1 barg. The catalyst is normally activated carbon. The heat of reaction is removed by circulating oil on the shell side of the tubular reactor cooling the phosgene gas supply pipe to typically 50 ºC.

Product purity of crude gaseous phosgene would typically be carbonyl chloride 97.5 wt%, with traces of chlorine and contaminants such as carbon dioxide, carbon monoxide, hydrogen chloride, oxygen and nitrogen making up the balance.

A caustic scrubbing system is used for neutralising phosgene and chlorine gas from vent and purge air streams and during upset conditions. Phosgene reacts slowly to give sodium carbonate and sodium chloride solutions. Same small phosgene unit packages have double containment with the containment space purged. Package units can include phosgene detectors for purge air from the double containment system.

Owing to the hazardous nature of phosgene common practice is to scrub the off-gas stream with a series of scrubbers with an additional scrubber provided to act as an emergency back- up.

Residual gases may be burnt to convert phosgene to carbon dioxide and HCl. One advantage is that other pollutants, such as solvents and CO, will also be combusted, however the combustion gases will contain HCl and will require scrubbing.

Releases to air

- Carbon monoxide, chlorine and phosgene from absorbers.
- Hydrogen chloride, carbon dioxide from combustion gases. Note: Phosgene hydrolyses only slowly in water,
- generating carbon dioxide and hydrogen chloride. Any release of phosgene to moist air can therefore contain these gases.

Releases to water

- Sodium carbonate, sodium chloride and sodium hydroxide in scrubber liquors.

Releases to land

- Spent catalyst from phosgene reactor.

2.1.5.6 Potassium iodide manufacture

Potassium iodide is produced by the reaction of potassium hydroxide with elemental iodine. Flake iodine charged as a solid is dissolved in potassium hydroxide solutions in a hooded mixing vessel. Where required, the potassium iodide produced is subsequently purified by crystallisation. Iodine dust and vapour (iodine readily sublimes because of its high vapour pressure at its melting point) that is released to the hood, principally during the charging operation, is scrubbed with a 3-4% potassium hydroxide solution. The resultant iodate liquor is recycled. The reaction is:

$3\ I_2 + 6\ KOH \text{ -------->} 5\ KI + KIO_3 + 3H_2O$

KIO_3 can be recovered as a useful co-product, by crystallisation. Alternatively it can be heated in a gas-fired furnace to produce additional potassium iodide:

$2\ KIO_3$ --------> $2KI + 3O_2$

The fused iodide is redissolved in water and purified by pH adjustment with CO_2. Barium carbonate, potassium carbonate, hydrogen sulphide and iron iodide are added to precipitate heavy-metal impurities and sulphates. The KI is then recrystallised.

Recovered iodine and potassium hydroxide scrubber liquors can be returned to process. This represents effective abatement of the iodine vapour.

Releases to air

- Iodine from absorbers.
- Flue gases, if gas firing is used for iodide recovery from iodate.

Releases to water

- Potassium hydroxide/ potassium iodide scrubber liquors during wash-down operations.

2.1.5.7 Sodium bromide manufacture

Sodium bromide solution is manufactured batchwise in general-purpose plant using sodium hydroxide and hydrobromic acid.

Hydrobromic acid is added to the reactor and reacts with the sodium hydroxide solution to form sodium bromide solution. Displaced vapours are vented to atmosphere via an aqueous scrubber, for recovery of the hydrogen bromide content. A caustic scrubber is used for absorption of residual contaminants and for emergency use.

Releases to air

- Hydrogen bromide from absorbers.

Releases to water

- Sodium hydroxide and sodium bromide plus other contaminants in spent absorber liquors.

Releases to land

- None.

2.1.5.8 Chlorine dioxide manufacture

This is the only chlorine oxide of commercial importance. It exists at ambient temperatures as a greenish-yellow gas (b.p. 11 ºC) and is a powerful oxidising agent. It is explosively unstable and has high toxicity.

Production of chlorine dioxide in the UK is on a small scale. However, it is a major tonnage chemical on a worldwide basis and virtually all bleached chemical pulp mills use one or more chlorine dioxide bleaching stages.

The explosive nature of the gas prevents its transportation It is therefore manufactured adjacent to its point of use and immediately absorbed in water (commonly at 6-10 g/ litre) for storage and process use.

The only economic route for the generation of chlorine dioxide in significant quantities is by the reduction of sodium chlorate in a highly acidic medium. The reaction consumes both the acid and reducing agents, which are therefore continuously added to the reaction vessel. Commonly available reducing agents are sulphur dioxide, hydrochloric acid or methanol.

Small-scale generation of chlorine dioxide

Chlorine dioxide can be generated in solution for the relatively low levels required by the textile and tallow industries, and for water purification purposes, by the oxidation of sodium chlorite. Gaseous chlorine is commonly used as the oxidising agent, although other agents can be used.

These small-scale uses can, however, give rise to gaseous chlorine dioxide in the working environment, which constitutes an atmospheric release.

Abatement systems are typically those used for handling chlorine.

Releases to air

- Losses of chlorine dioxide from absorbers.
- Hydrogen chloride and chlorine.

2.1.5.9 Methyl chlorosilanes and siloxane polymer manufacture

Methyl chlorosilanes are produced by the reaction of silicon and methyl chloride, and are then hydrolysed to give silicone hydrolysis polymers. The process stages are: reaction, distillation and hydrolysis. The hydrolysis step also produces hydrogen chloride. The basic silicone polymer mixture from hydrolysis is further processed to give a range of silicone products, including emulsions, elastomers, fluids and resins.

The main reaction takes place in the presence of a copper catalyst at 270-300 ºC under ambient pressure conditions in a fluidised-bed reactor. Vapours from the reaction vessel and distillation are condensed and returned to their origin using vent condensers (water or cryogenic).

Over 97% of the hydrogen chloride produced in hydrolysis is recovered, recycled and reacted with fresh methanol to produce methyl chloride. This is supplemented with fresh methyl chloride for the feed to the reaction vessel to make up the balance.

Within the process there is the potential for emissions of hydrogen chloride, methyl chloride, methane, dimethyl ether and chlorosilanes. Vents from process plant and intermediate storage tanks pass through a cryogenic condenser and distillation unit for recovery. Inerts from the cryogenic distillation system pass to an energy recovery unit where the combustible components are burnt, and residual hydrogen chloride is scrubbed out using water.

Chlorosilane storage tanks are maintained under a nitrogen blanket and are vented to the recovery system.

All aqueous arisings pass through an on-site effluent treatment plant for neutralisation and separation of solids (which are disposed of either by landfill or by incineration), followed by a biological treatment step for the removal of organic materials.

Releases to air

- Silicones, VOCs and hydrogen chloride from condensers nd scrubbers (process and storage tanks).

Releases to water

- Hydrogen chloride, silanols and hydrolysate in spent absorber liquors.

Releases to land

- Sludge from the effluent treatment plant.
- Spent neutralised reaction mass.
- By-product solid siloxanes.

2.1.6 Titanium dioxide

2.1.6.1 Titanium dioxide manufacture - Sulphate process

2.1.6.1.1 Introduction to the "sulphate" process

There are two commercial processes for the manufacture of titanium dioxide (TiO_2), both of which are the subject of an EC Directive on the harmonisation of programmes to reduce and eventually eliminate pollution caused by waste from the TiO_2 industry (see **Ref 24**). One process is the "chloride" process, which is described in **Section 2.1.6.2**, and the other is the "sulphate" process - which is described in this section.

The sulphate route uses sulphuric acid to digest prepared titanium dioxide ore which can be from low-concentration ores such as ilmenite but can also be higher-concentration synthetic slags. The greater the presence of impurities, however, the more the solid waste from the process. Both crystalline forms of TiO_2 can be readily formed.

The process generally consists of the following sequential stages (see **Figure 2.17**, for a typical block flow scheme).

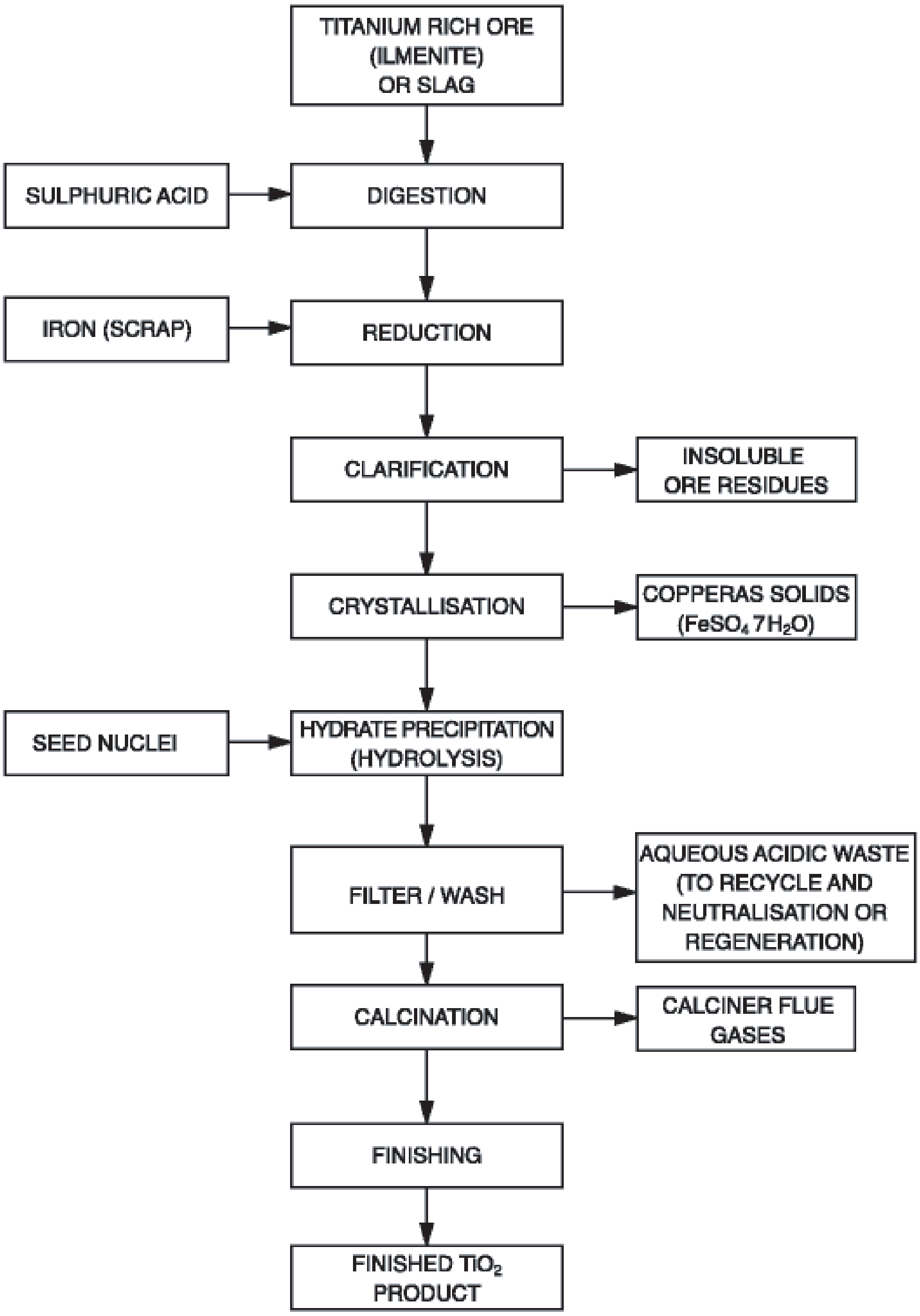


Figure 2.17: Outline flow diagram (Sulphate process)

2.1.6.1.2 Digestion

The raw ore is usually dried and then ground to produce the optimum particle size (typically 40-60 micron) for efficient dissolution with concentrated sulphuric acid.

The ground ore is mixed with concentrated sulphuric acid in a digester (which is usually a batch operation but some digesters are continuous).The strongly exothermic reaction is initiated by the introduction of a measured quantity of steam and takes place at around 150 ºC

The equation for the digestion reaction may be summarised as:

$FeTiO_3 + 2\ H_2SO_4$ ------> $TiOSO_4 + 2\ H_2O + FeSO_4$

During the batch process the reaction raises the temperature of the reactor from 180 to 200 ºC and great care has to be taken to ensure that the reaction does not run away. Agitation/ mixing of the reactor is generally achieved by air blowing. As well as steam, the off-gas contains sulphur dioxide, which must be scrubbed.

A solid 'cake' forms in the digester towards the completion of the reaction, and this is subsequently dissolved in cold water. The primary product from the reaction is titanyl sulphate ($TiOSO_4$) but both ferrous and ferric sulphates are produced as by-products.

2.1.6.1.3 Reduction, clarification and crystallisation

The digester liquor is contacted with scrap iron to convert ferric (Fe^{3+}) ions to ferrous (Fe^{2+}), otherwise the iron would remain with the TiO_2 throughout all subsequent processing stages.

Any suspended material is removed from the solution by flocculation and filtration. It is washed with water to recover the acid. The solid residue is neutralised with limestone before going to landfill. The acidic liquors are recycled back to the process.

The clarified solution may be sent to batch cooler-crystallisers to remove the bulk of the iron sulphate as solid, where ilmenite is the feedstock. This solid is used in water treatment, pharmaceutical and pigment industries.

The iron-depleted product liquor is polished using candle filters to remove fine particles and finally concentrated in evaporators.

2.1.6.1.4 Hydrolysis, precipitation, filtration and leaching

Hydrated titanium dioxide is produced by hydrolysing the liquor with steam in rubber-lined mild steel vessels.

The hydrolysis reaction is:

$TiOSO_4 + 2\ H_2O$ --> $TiO(OH)_2 + H_2SO_4$

Precipitation of the hydrated TiO_2 is achieved by boiling the liquor for some hours followed by cooling to 60 ºC. The addition of the correct TiO_2 nuclei to the batch determines the final crystal form of the titanium dioxide (anatase or rutile crystals).

The precipitate is washed and dried on vacuum filters to remove trace metal salts.

The resultant solid is slurried with dilute sulphuric acid, and zinc or trivalent titanium is usually added as a reducing agent. The slurry is 'leached' at 50 ºC to remove final traces of iron and undergoes final washing and drying. Conditioning agents are added at this point to the resulting pulp to enhance crystallite growth.

The filtrate is strongly acidic and the sulphuric acid can be re-concentrated and recycled back to the process or neutralised with lime/ limestone and the product gypsum sold for plasterboard manufacture etc.

2.1.6.1.5 Calcination and solids processing

In the calcination stage, water and some oxides of sulphur are expelled from the hydrated titanium dioxide pulp. The rotary kilns are directly fired with oil or gas, the pulp moving under gravity counter-currently to the combustion gases, and temperature control is critical to the production of the correct crystalline form of the pigment.

The crystalline TiO_2 product is cooled, milled, coated, micronised and then packed. Two stages of milling are used:

- dry milling to break down up to 20 mm agglomerates from the calcining process to 75-100 microns; and then
- wet milling to achieve fine particles to the correct size for optimum pigment properties (0.2-0.4 microns).

The TiO_2 particles are coated with other oxides (eg aluminium/ silicon/ zirconium) to improve durability and may be coated with organic materials to promote dispersion. - and these may affect the toxicity classification of the final product (TiO_2 itself is classed only as a nuisance dust).

2.1.6.1.6 Releases from the "sulphate" process

The sulphate process has the potential to produce large quantities of aqueous effluents including metal sulphates and dilute sulphuric acid. Large-scale co-production of useful saleable by-products from this effluent is possible and would minimise the quantity of effluent released to the environment. This waste minimisation approach constitutes BAT and may include the following:

- ferrous sulphate being re-converted to the ferric form, which is used in water treatment.
- spent sulphuric acid being either regenerated or treated with chalk or lime to produce white gypsum (for wallboards) and red gypsum (agricultural use).
- the high-quality CO_2 produced during gypsum manufacture may be condensed and sold (e.g. for carbonated drinks).

Abatement of oxides of sulphur releases resulting from reaction of the ore with sulphuric acid is via the processes described in **Section 2.1.2**.

Releases to air

- Oxides of sulphur from the digesters.
- Oxides of sulphur from the calcination kilns.
- Particulate matter from kilns, dry milling and materials handling.

Releases to water

- Liquid effluent from solids washing.
- Liquid effluent after by-product production.

Releases to land

- Unreacted ore and residue from the digesters.

- Solids from acid neutralisation processes.

2.1.6.2 Titanium dioxide manufacture - Chloride process

2.1.6.2.1 Introduction to the "chloride" process

As stated in **Section 2.1.6.1** titanium dioxide is produced by either the "sulphate" process or the "chloride process". In the chloride process, chlorine gas is used as an intermediary in the process and is recovered for re-use. The chloride process can treat a wider range of ores than the sulphate process including natural rutile (95% TiO_2), synthetic rutile (93-96% TiO_2) and lower-concentration ores. Higher-concentration ores are preferred to minimise chlorine losses, because impurities, such as iron in the ore feed result in a net loss of chlorine. Significant quantities of make-up gas are required.

A schematic block diagram illustrating the primary processing stages is given in **Figure 2.18**.

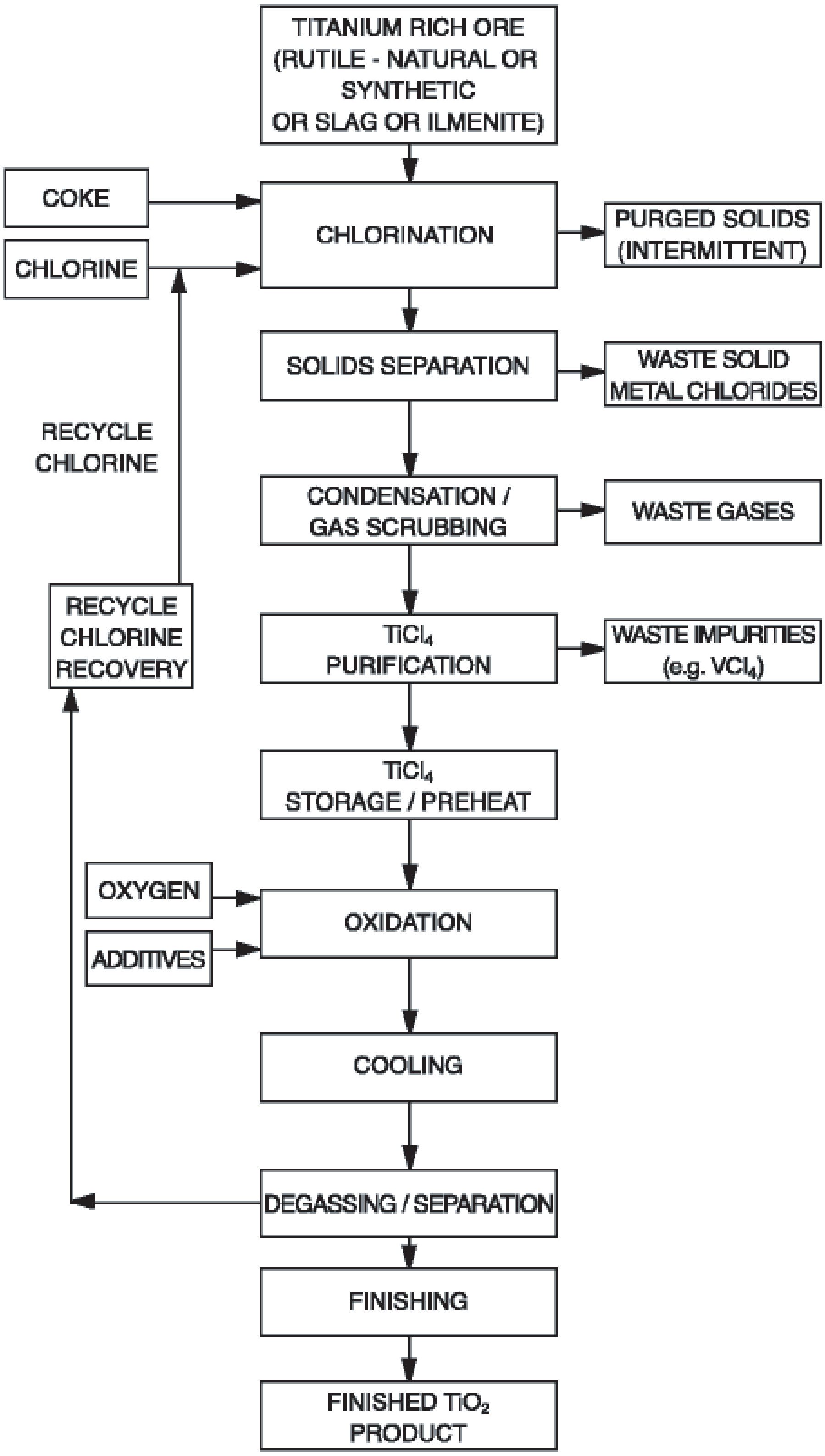


Figure 2.18: Outline flow diagram (Chloride process)

2.1.6.2.2 Chlorination

Ore containing titanium dioxide, and coke are fed to a fluidised-bed reactor where an exothermic reaction with chlorine gas takes place at 1000 ºC The primary reaction is:

$2\ TiO_2 + 4\ Cl_2 + 3\ C \text{ ------=> } 2\ TiCl_4 + 2CO + CO_2$

Impurities such as iron oxide will react in a similar manner:

$FeO + Cl_2 + ºC \text{ -------> } FeCl_2 + CO$

Impurities such as silica and zirconium do not chlorinate and may remain accumulated in the reactor. There is however a natural attrition/ carry-over of fines along with the off-gases, and this may be sufficient to prevent build-up. Otherwise the solids will require periodic removal. The reactors require total bed replacement about once per year.

The resulting vapours of titanium tetrachloride plus other volatile metallic chloride impurities are cooled with recycled cold $TiCl_4$, which allows removal of some impurities. The gas stream is then condensed and pumped to a dedicated storage facility.

Further purification by distillation is carried out and the distillate product stored.

From storage, the liquid titanium tetrachloride is heated and reacted with oxygen at around 1500 ºC to yield chlorine and titanium dioxide powder. These are cooled and the powder is collected in bag filters.

2.1.6.2.3 Oxidation

Oxidation of the $TiCl_4$ to titanium dioxide and chlorine is carried out at between 1000 and 1500 ºC in a plasma arc furnace, using oxygen injection. The reaction involved is:

$TiCl_4 + O_2 \text{ --------> } TiO_2 + 2\ C1_2$

The oxidation phase is used to control the final quality of TiO_2 crystal size for the pigment. The oxidation products are a mixture of chlorine and oxygen gases and titanium dioxide powder. These are quenched after exiting the reactor, normally by indirect water cooling. The titanium dioxide is slurried with water and transferred to the finishing stage. Finishing treatment is similar to that of the sulphate process, including conditioning with additives. Chlorine is separated in one of two ways. In the first (the older process) chlorine is absorbed/ desorbed in liquid titanium tetrachloride before being returned to chlorination. In the second process the chlorine from oxidation is directly recycled to chlorination. The basic processing stages are similar.

(a) Absorption/desorption process

In the oxidation stage of the older process, the oxide is separated from the carrier gas, which is predominantly chlorine. The oxide is slurried in water and sent for finishing. The chlorine gas is drawn from the filters and then absorbed in liquid titanium tetrachloride in an absorption column. This liquid is stored, whilst the tail gases pass to a caustic scrubbing train, to remove residual chlorine, with inerts passing to the main process stack.

Chlorine is recovered by desorption from the liquid titanium tetrachloride. The recycled chlorine is liquefied and stored or directly used in the chlorination section.

(b) Chlorine recycle process

This process involves direct recycle of chlorine from oxidation to chlorination, by operation of the oxidation reactors at a higher pressure than the chlorinators.

2.1.6.2.4 Abatement systems for gases

Off-gases from chlorination that include carbon monoxide, carbon dioxide with some hydrogen chloride and titanium tetrachloride pass through the scrubbing train. Aqueous scrubbers absorb the HCl and then caustic scrubbing removes any chlorine that may 'slip' from the reaction stage. This is achieved either using a dedicated caustic scrubber with back-up caustic injection available or by injection of caustic into an aqueous scrubber in the event that chlorine is detected. Sodium hypochlorite produced can either be sold or destroyed catalytically before discharge. It is practicable to produce sales-grade hydrochloric acid in the first stage of scrubbing using demineralised water.

All other venting and reliefs from the process and storage areas are scrubbed with caustic soda solution to make hypochlorite.

Thermal oxidisers have been installed on some plants to convert carbon monoxide in the tail-gas to carbon dioxide, to reduce the toxicity of the discharge gases- one of the main problem areas for the Chloride process.

2.1.6.2.5 Abatement systems for liquids

Metal chlorides and coke from the reaction stage can be treated either by neutralisation with lime, resulting in metal hydroxide precipitates which are filtered and landfilled, or by converting these wastes into by-product hydrochloric acid and metal oxides. The conversion to oxide process involves roasting the metal chlorides in air to form HCl and leaving the oxide as a solid. The process has potential for producing a relatively inert oxide with sales potential (e.g. as an inert filler in bricks or blocks), and it also allows recovery of hydrochloric acid rather than the chloride value being lost as chloride ion in the effluent stream - but despite some energy recovery through steam production in waste heat boilers, the process can be significantly more costly than simple neutralisation and disposal.

2.1.6.2.6 Abatement systems for solids

Waste solids from the chlorination stage, which mainly include metal chlorides, coke and some ore, are neutralised in a wet chalk-lime slurry. The metals are precipitated as hydroxides. The filter cake is landfilled and the aqueous filtrate is discharged to estuarial waters.

Sand may be used to scour titanium dioxide from the oxidation cooler. It is then separated through lock-hoppers and sent to landfill, or re-used.

2.1.6.2.7 Releases from the "chloride" process

Releases to air

- Hydrogen chloride from absorbers.
- Chlorine from absorbers and storage tanks.
- Titanium tetrachloride from storage, etc. vents. (It is common practice is for vents from items of $TiCl_4$ equipment to be manifolded to a vent header and drawn through an aqueous scrubber by an induced draught fan. Separate maintenance areas are ventilated via aqueous or caustic scrubbers.)
- Carbon monoxide/ carbon dioxide tail gas emissions to stack, (Percentage of CO varies between 20 and 40%, unless oxidised to CO_2).

Releases to water

- Hydrochloric acid from aqueous scrubbers.

- Aqueous waste from neutralised effluent treatment.
- Filtrate from lime neutralisation effluent treatment filtration.
- Sodium hypochlorite from caustic scrubbing.

Releases to land

- Metal hydroxides filtered out from lime neutralisation effluent treatments.
- Metal oxides from effluent treatment plant.
- Inert materials from chlorinator beds.

2.1.7 Ammonia production

2.1.7.1 Introduction

Ammonia is manufactured by the catalytic reaction of nitrogen and hydrogen. The basic reaction is:

$N_2 + 3\ H_2\ <====>\ 2NH_3$

Nitrogen is extracted from air by air liquefaction or, by burning out the oxygen. Hydrogen is produced from several sources, including:

- steam reforming of natural gas or light hydrocarbons;
- partial oxidation of fossil fuel feedstocks from petroleum to natural gas; and
- by-product hydrogen from plants making other chemicals.

Current production in the UK is based on steam reforming of natural gas. The processes are highly integrated to optimise material and thermal efficiencies, and three main alternatives are as follows:

2.1.7.2 Conventional steam reforming

Ammonia production from steam reforming of natural gas involves the following process stages:

- desulphurisation; primary reformer;
- secondary reformer;
- CO shift conversion;
- condensation;
- carbon dioxide absorption;
- methanation and final purification;
- ammonia synthesis; and storage.

A flowchart of the process is shown in **Figure 2.19**.

2.1.7.2.1 Desulphurisation

To avoid poisoning of the reformer catalysts, sulphur compounds in the natural gas feedstock are removed to below 0.15 mg/m^3. For this purpose the gas is heated to 350-400 °C, usually in the primary reformer, and then passed with a small hydrogen stream across a cobalt-molybdenum catalyst. The sulphur compounds are hydrogenated to hydrogen sulphide which is then absorbed in a layer of pelletised zinc oxide. The resulting zinc sulphide remains in the reactor and is periodically removed for regeneration or disposal. The hydrogen for the reaction is usually recycled from the synthesis section.

2.1.7.2.2 Primary reformer

The compressed desulphurised gas is mixed with steam and passed to the primary reformer where it is converted to carbon monoxide and hydrogen over a catalyst at ca. 850 ºC. The reformer catalyst is usually nickel-based and supported on porous alumina, and has a life of around four years. The optimum steam:carbon molar ratio depends on factors such as feedstock quality, purge gas recovery, primary reformer capacity, shift operation and the plant steam balance, but is typically around 3 for a BAT reforming process.

The composition of the gas leaving the primary reformer is given by close approach to the following chemical equilibria:

$CH_4 + H_2O \ < ====> \ CO + 3\ H_2$

$CO + H_2O \ < ====> CO_2 + H_2$

The process is endothermic and energy is supplied by firing in a radiant furnace. Part of the natural gas supplied to the plant is used as fuel in the furnace, together with purge gas from the synthesis stage. The combustion gases, at a temperature of 1000-1100 ºC, are used to provide heat for a number of process streams in the reformer convection section, and the flue gas leaving the convection section (at 100-200 ºC) is the main source of emissions from the plant.

2.1.7.2.3 Secondary reformer

Only 30-40% of the hydrocarbon feed is converted in the primary reformer because of the equilibrium composition at the actual operating conditions. The temperature must be raised to increase the conversion and this is achieved in the secondary reformer by combustion of the gas with process air, which also provides nitrogen for the final synthesis gas.

Process air is compressed to the reforming pressure, heated further to 600 ºC and then passed with the primary reformer gas over a nickel-containing catalyst. The secondary reformer outlet temperature is around 1000 ºC and approaching 99% of the hydrocarbon feed (to the primary reformer) is converted. The process gas is then cooled to 350-400 ºC in a steam-raising boiler or superheater before passing to the shift-reactor.

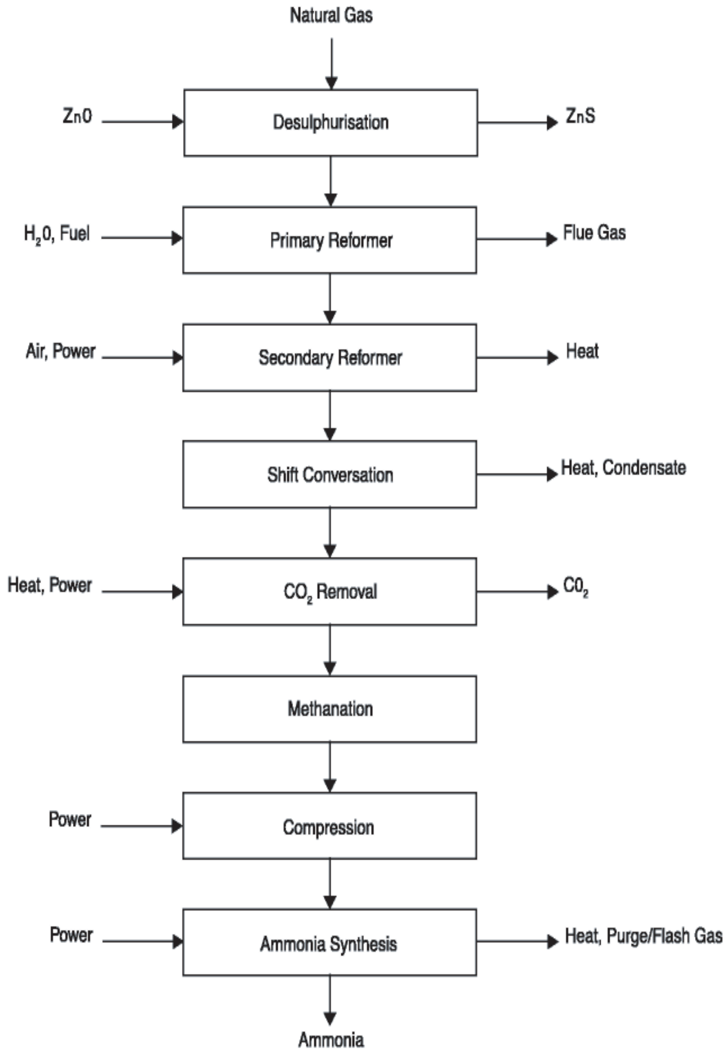


Figure 2.19: Steam/air reforming process for ammonia

2.1.7.2.4 CO shift conversion

The process gas from the secondary reformer contains 12-15% CO and most of this is converted to carbon dioxide by injection of steam in the two-stage shift section, according to the following reaction:

$CO + H_2O <====> CO_2 + H_2$

In the high temperature-shift (HTS) stage, the gas is passed through a bed of iron oxide/ chromium oxide catalyst at around 400C, before being cooled and passed through the low-temperature shift (LTS) converter, which is filled with a copper oxide / zinc oxide-based catalyst. The residual CO content in the converted gas stream is approximately 0.2-0.4% CO.

2.1.7.2.5 Condensation

The process gases are cooled, usually by heat exchange with other process fluids for heat recovery, to condense out the water vapour. The heat released during cooling/ condensation is typically used for the regeneration of the CO_2 scrubbing solution, or driving an absorption refrigeration unit; and/or for boiler feedwater preheat.

The condensate produced is the main liquid effluent from an ammonia plant.

2.1.7.2.6 Carbon dioxide absorption

After water vapour removal, the carbon dioxide component, which is ca. 17-19% of the process gases, is removed by one of the following:

- absorption in a solvent, such as methanol. The absorbent is then primarily regenerated by reducing the pressure and allowing the carbon dioxide to desorb.
- chemical reaction with a reagent. The most widely used reagent is monoethanolamine solution (with inhibitors to protect against excessive reagent degradation and corrosion) which is recovered by heating with low-pressure steam to reverse the reaction. This operation is a major consumer of low-pressure steam.
- physical adsorption. Pressure-swing adsorption (PSA) systems rely on the use of selective adsorbents. Individual components of the mixed gas stream are preferentially adsorbed at high pressure and then desorbed by reducing the pressure, and possibly purging, in a cyclic process. PSA systems are particularly useful where it is necessary to remove excess nitrogen as well as carbon dioxide.

For new ammonia plants the following CO_2 removal processes give residual CO_2 concentrations in the range 100 - 1000 ppmv. and may be regarded as BAT:

- AMDEA standard two-stage process, or similar.
- Benfield process (HiPure, LoHeat), or similar.
- Selexol or similar physical absorption processes.

2.1.7.2.7 Methanation and final hydrogen purification

Most carbon dioxide is removed in the previous stage but to prevent poisoning of the ammonia synthesis catalyst, residual oxides of carbon are reduced to just a few parts per million by conversion to methane (methanation) at 300-400C with the aid of a supported nickel catalyst. This is required. The reaction is:

$CO_x + (2 + x)\ H_2 \text{ —-> } CH_4 + x\ H_2O$

Further purification of the feed gas can also include:

- dehydration - with molecular sieves; and
- removal of nitrogen, methane and inerts, eg argon. - by cryogenic treatment.

2.1.7.2.8 Ammonia synthesis

The synthesis of ammonia from the mixture of nitrogen and hydrogen (synthesis gas) takes place on a porous catalyst containing ferrous and ferric oxides with promoters such as potassium, aluminium, calcium or magnesium oxides, at pressures usually in the range of 100-250 bar and at temperatures in the range of 350-550 °C according to the reaction:

$N_2 + 3\ H_2 <====> 2\ NH_3$

Ammonia synthesis is exothermic, and only 20-30% of the reactants are converted per pass as a result of the unfavourable equilibrium conditions - so the ammonia component has to be removed and the unreacted raw materials recirculated. Ammonia is condensed from the gas by sequential heat exchange culminating in ammonia-refrigerant cooled condensers, and the liquid is transferred to storage as product.

Synthesis gas is normally added to the loop upstream of the final condensers so that water and other minor impurities are washed out with product ammonia, and the cold gas from the ammonia separation stage is reheated by a heat exchange train, boosted in pressure by the circulating compressor, and returned to the conversion catalyst beds.

A purge is taken off the loop to prevent the accumulation of inerts like methane or argon. This purge gas is usually water-washed or chilled to recover ammonia and is then used as fuel gas in the primary reformer. Recovery of hydrogen by PSA or the use of cryogenic schemes to recover many components are also practised commercially.

Steam-reforming ammonia plants have a high-level of surplus heat available for steam production in the reforming, shift conversion and ammonia synthesis sections, and in the convection section of the primary reformer. Most of this heat is used to raise high-pressure steam for use in turbines for driving the main compressors and pumps followed by export as medium- and low-pressure process steam. A modern steam reforming ammonia plant can be made totally energy self-sufficient if necessary but arrangements with some steam export and some electricity import are generally preferred on the grounds of flexibility.

2.1.7.3 Hydrogen feed gas variants

2.1.7.3.1 Excess-air secondary steam reforming

Some processes are designed for reduced primary reforming and greater duty in the secondary reformer to off-set the low efficiency of the primary reformer. The main features of such systems are:

- decreased firing in the primary reformer;
- increased process air flow to the secondary reformer;
- cryogenic final purification after methanation; and
- lower inert level of the make-up synthesis gas.

Decreased heat supply in the primary reformer means that the process outlet temperature is lowered (to about 700 °C), the firing efficiency increases, and the size and cost of the primary reformer are reduced. The milder operating conditions prolong catalyst, catalyst tube and outlet header service lives. The extent of reforming is reduced in line with the lower heat supply and lower temperature. Generally a slight decrease in steam to carbon ratio is acceptable, compared to the conventional concept.

Decreased heat supply in the primary reformer also means that increased internal firing in the secondary reformer is necessary to achieve approximately the same degree of total reforming. A somewhat higher methane slip, and thus a lower secondary reformer outlet temperature, is acceptable and preferable in this type of process, as methane is removed in the final purification step.

The process air requirement is about 50% higher than in the conventional process, which means increased compression capacity and energy demand. The process air compressor is usually driven by a gas turbine with the exhaust then used as combustion air in the primary reformer. Some excess steam is available for export when using a gas turbine.

In the cryogenic purifier all the methane and all the excess nitrogen are removed from the synthesis gas as well as part of the argon. The cooling is produced by depressurisation and no external supply is needed. The purified synthesis gas is then practically free of all impurities, except for a small amount of argon. The cryogenic unit also receives the purge from the synthesis section and delivers an off-gas for fuel.

The removal of essentially all impurities from the make-up synthesis gas is a significant improvement, compared to the conventional purification by methanation only. Higher conversion per pass and reduced purge flow together result in a more efficient process.

2.1.7.3.2 Non-fired primary reformer/auto-thermal reforming

Lower emissions to air may be achieved with processes that use an excess of air in the secondary reformer. The hot gas from the secondary reformer is used as the heat source for the primary reformer. The primary reformer is therefore a heat exchanger instead of a fired furnace.

Low-temperature hydrodesulphurisation is employed, as this permits preheating by steam rather than by a fired heater.

Instead of supplying process steam to the primary reformer and removing condensate after the shift reaction, a saturator/desaturator system is employed. Water is evaporated into the gas stream in the saturator vessel and is condensed from the gas stream in the desaturator vessel downstream of the shift converter. The condensate is then recycled to the saturator after heating in the shift converter. Although most of the process steam is provided by the saturator/desaturator loop, some addition of steam is needed. A purge of condensate is also required.

A single medium-temperature shift converter replaces the conventional two-stage system.

A pressure swing adsorption unit is used to remove the comparatively large excess of nitrogen, with carbon dioxide and part of the inerts.

Ammonia synthesis is carried out at relatively low pressure. It is necessary to dehydrate the synthesis gas due to the sensitivity of the low-pressure catalyst to water.

No treatment of purge gas from the loop is required. It returns to the reformer section upstream of the saturator vessel.

2.1.7.3.3 By-product hydrogen feed

By-product hydrogen from other processes may be used for ammonia synthesis.

The crude by-product hydrogen passes through a nitrogen wash unit, which both adds the required nitrogen and removes the carbon monoxide impurities in the crude hydrogen. This stage is followed by a conventional compression and ammonia synthesis section. The inerts in the gas are low so that only a small purge is required for the synthesis loop.

The reject gas from the nitrogen wash, containing the carbon monoxide and methane removed from the hydrogen gas, may be burned as fuel for the steam superheater.

2.1.7.3.4 Comparison of reforming techniques

Processes using a non-fired primary reformer, or those processes where excess air is introduced into the secondary reformer to offset the energy requirements of the primary reformer, are likely to be regarded as best practice for new plants using steam reforming. However, adaptation of conventional plants, with their very tightly integrated steam/ power systems, would generally be very expensive.

2.1.7.4 Potential release routes from ammonia production processes

Potential release routes for all four variants described above, are given below.

Releases to Air

- Carbon dioxide, plus entrained absorption liquid, from carbon dioxide removal plant.
- Carbon monoxide, carbon dioxide, hydrogen, methane and ammonia from several stages of the process during start-up.
- Pressure relief vents with the potential for emissions of ammonia, hydrogen, carbon monoxide, carbon dioxide and methane.
- Ammonia from various other sources, e.g. vent from process condensate stripper unless recycled, degassing of compressor seal oils, and vents from tanks that contain ammoniated liquors.
- Oxides of sulphur, nitrogen and carbon from flue gases of the primary reformer.

Particulate emissions should not arise except when replacing catalysts or starting the process. Appropriate procedures should be operated to avoid any particulate emissions.

Releases to water

- Process condensates from condensation between shift reactors and absorption of carbon dioxide, and from carbon dioxide overheads. These condensates can contain ammonia, methanol, methylamines, dimethylamines and trimethylamines.
- Condensate from synthesis gas compression, contaminated with lubricating oils.
- Spills from the carbon dioxide removal system. A wide range of reagents and solvents may be present, including potassium carbonate, organic amines and methanol.
- Regeneration liquors from ion exchange resins containing trace amounts of mercury.
- Blow-downs from cooling towers.

Releases to land

- Catalysts and solid reagents, typically from following processes:
- desulphurisation (various, e.g. zinc sulphide);
- primary reformer (nickel on refractory);
- secondary reformer (nickel on refractory);
- high-temperature shift (iron oxide, chromium promoter);
- low-temperature shift (copper-based);
- methanator (nickel based); and
- synthesis converter (iron oxides).

These should be regenerated or recovered off-site with only residual disposal to land.

- Regeneration sludges from recovery of carbon dioxide absorbent from spent solution.
- Spent ion-exchange resins.

2.1.7.5 Control of releases arising from ammonia production

2.1.7.5.1 Control of gaseous releases

(a) Flue gas emissions from primary reformers

Complete elimination of a fired primary reformer has been achieved with one process. It may not be commercially appropriate for other existing processes.

Flue gas from a fired primary boiler is substantially similar to that of normal combustion of fuels. General principles of control techniques are common to those of combustion plant (see IPC Guidance Note S2 1.01 (**Ref 21**).

(b) Carbon dioxide

The quantity of carbon dioxide removed from the process gas depends on the process selected. Some beneficial uses are possible, for example, sales to the brewing and soft drinks industry.

(c) Ammonia

Ammoniated vents occur from several sources and the ammonia is controlled by absorption, condensation, incineration and containment. These techniques are discussed in **Section 2.2.1.2**.

Containment of ammonia is an important aspect of controlling releases. Possible techniques include the following:

- Use of vapour balance lines for the transfer of ammonia between storage and transport container, or a refrigeration unit to condense vapours from both storage and transport containers.
- Purging of loading lines with nitrogen.
- Full height bunding of ammonia storage tanks with cover of annular area.
- High-integrity mechanical design for items such as flanges, pump seals, and valve stem packing.
- Facilities to empty equipment of liquid ammonia and to purge ammonia vapour through control devices such as condensing refrigerators before opening for routine or emergency maintenance.
- Tiled areas should be employed to contain spillages from the carbon dioxide recovery unit and foaming from the desorber and to allow these liquors to be returned to the process.

2.1.7.5.2 Control of aqueous releases

Steam stripping techniques are used to remove volatile organic components dissolved in aqueous effluent streams - but very often the resultant gaseous streams also requires treatment.

Process condensate should be stripped to reduce the ammonia content to 10 mg/1, unless the condensate passes to a treatment plant in which recovery is jointly performed on a number of ammoniated liquors. Steam stripping typically removes about 99% of the ammonia from a waste stream, and the potential for releases into water generally arises from inadequate stripping performance.

Use of medium-pressure steam as the stripping medium will allow this stream to join the reformer feed, reducing the volume of aqueous discharge.

Care should be taken when selecting construction materials, particularly for the column overhead equipment, since severe corrosion can be encountered. Effluent steam strippers are prone to plugging and sequestering agents are frequently used to prevent calcium salt deposition.

2.1.8 Activities using or releasing Ammonia

2.1.8.1 Control of ammonia releases

Ammonia safety and handling

Two basic methods are currently used for storage of anhydrous ammonia, the choice primarily depending on the quantity to be stored:

- Storage at ambient temperature and the equivalent vapour pressure in cylindrical vessels for quantities up to about 500 tonnes and in spheres for larger inventories.
- Ammonia may be stored at atmospheric pressure in cylindrical flat-bottomed tanks by keeping it at its boiling point (-33 ºC). This method of storage is considered economical when the inventory approaches 5000 tonnes.

The storage of anhydrous ammonia is covered by an HSE guidance document, HS(G) 30 (**Ref 25**) which details basic requirements for the design and operation of spherical and cylindrical pressure vessels and associated equipment. Information on storage and off-loading techniques is also available in company publications:

A few important properties of ammonia are:

- Ammonia gas is colourless but pungent; the detectable odour limit for ammonia is around 5 ppm by volume so it serves as its own warning agent;
- Ammonia combines with mercury to form explosive compounds, so instruments containing mercury must not be used if ammonia can come into contact with the mercury.
- Ammonia will not readily attack carbon steels, but reacts strongly with copper and alloys containing copper.
- The flammable limits of ammonia are from 16 to 25% by volume in air, with an auto-ignition temperature of 651 ºC

2.1.8.1.1 Absorption of ammonia

Ammonia is very soluble in water (though the process is exothermic) so water is the normal absorption medium. Practicable absorbers have been based on all the common techniques - packed or tray columns, venturis, jet scrubbers, etc.

The scrubber liquor is a potential waste stream, but it can be stripped with steam or air to recover the ammonia for beneficial use. Where high ammonia concentrations are required so that it can be used beneficially elsewhere, multi-stage countercurrent absorption, and/or cooling of the circulating absorbent and/or the use of elevated pressure should be used.

The use of sulphuric acid in the final scrubbing stage will achieve very low release concentrations and the resultant ammonium sulphate solution may be of value in the fertilizer market.

2.1.8.1.2 Condensation of ammonia

Ammonia condenses at around -33 ºC at atmospheric pressure so can be condensed by refrigeration, particularly at elevated pressures. The effectiveness of ammonia recovery will depend on the inerts content of the waste gas as well as the pressure and the temperature to which it is cooled.

2.1.8.1.3 Incineration of ammonia

Ammonia is combustible but has a relatively narrow flammability envelope of 16-25% in air, and its combustion has the disadvantage of producing NO_X. In practice, incineration needs to be supported by the combustion of other components so, if not present in the waste, there is a requirement for auxiliary fuel.

Condensation and wet scrubbing are generally preferred for end-of-pipe control of ammonia emissions to atmosphere. However, emergency or start-up vents may be an exception and properly designed flares or vents to a safe location may be appropriate for short-duration emissions.

2.1.8.1.4 Catalytic oxidation of ammonia

Available ammonia can be oxidised at 150 -250 °C over precious metal catalysts to forming nitrogen and water.

A support fuel is generally needed to maintain the required catalytic reaction temperature, and periodic replacement of the catalyst is required. Catalyst poisons and particulates are undesirable species so should be avoided in (or removed from) the ammonia-containing stream to be treated.

2.1.8.2 Ammonia recovery

2.1.8.2.1 Ammonia stripping

Ammonia is recovered by stripping from weak solutions resulting from other processes. The stripped gas may be dried and then used in other processes, but more often it is recovered as strong ammonium hydroxide (s.g. 0.880).

To achieve maximum recovery of ammonia, strong alkali (usually calcium or sodium hydroxide) is added to the ammonia-containing solution to raise the pH to about 9. The solution is then pre-heated by heat exchange with stripped liquor and the ammonia removed by steam stripping. The product gas stream containing ammonia and steam is cooled to condense out an ammonia solution, the lower the temperature, the lower the NH_3 vapour pressure of the solution - and a temperature of about 5 ºC is typical for the production of 0.880 ammonia. The residual tail-gas stream is scrubbed before discharge to air.

Depending on the process the recovered ammonia solution may be treated with activated carbon to remove contaminants.

2.1.8.2.2 Potential release routes from ammonia recovery processes

Releases to air

- Ammonia from scrubber.

Releases to water

- The stripped liquor from the stripping column, which contains alkali and ammonia.
- Spillages.
- Contamination of cooling water by leaks.

Releases to land

- Spent activated carbon filters.

2.1.8.3 Manufacture of Sodamide

2.1.8.3.1 Production of sodamide

Sodamide is produced both for sale and for direct use. The more usual process is a dry process using molten sodium which is described below, but there is an alternative solvent-based process.

Sodium is melted under a nitrogen blanket in the reaction vessel which is fitted with overpressure protection and any emergency relief is vented to a containment vessel from which the gases are discharge at high level. Anhydrous ammonia is fed into the reactor at a controlled rate where it reacts with the sodium to form sodamide. The reaction is exothermic and the temperature is controlled by regulating the rate of addition of ammonia, together with external cooling applied to the reactor. The reaction is:

$2\ Na + 2\ NH_3$ -----------> $2NaNH_2 + H_2$

An excess of ammonia is used and this, together with hydrogen generated in the reaction, passes to flare-stack - particulate sodamide carried over with the exit gas matter having been removed from the gas stream by passing through a seal pot. To minimise entrainment of sodamide in the gas stream and to prevent any ingress of air, forced extraction from the reactor is not used.

To maximise destruction of ammonia, a supplementary flame of natural gas is employed which is similar to a conventional flare stack's igniter, but with a larger flame. The combustion area should be fitted with a wind shield and a flame failure device which automatically prevents ammonia feed to the reactor when the flare stack is not fully operational.

As both sodium and sodamide react violently with water, the use of water on the plant is severely restricted. Where the sodamide product is isolated, solidified and packed it is conveyed using recirculated nitrogen (prolonged contact of sodamide with dry air can give rise to the formation of peroxides) with some nitrogen bled off and discharged to air via a water scrubber. The liquid effluent from this scrubber may contain small amounts of sodium hydroxide solution resulting from any carry-over of sodamide.

Maintenance of the plant may generate material contaminated with sodamide - and steam and water spray techniques are used, resulting in a sodium-hydroxide-contaminated aqueous effluent. Oil used for sealing the reaction vessel will slowly become contaminated with sodamide and need reclamation or replacement, with the contaminated oil being treated on-site to remove any sodamide and then being recovered or disposed of via a waste contractor.

2.1.8.3.2 Potential release routes from the sodamide process

Releases to air

- Ammonia and sodamide from pressure relief.
- Ammonia and oxides of nitrogen from the flare.

Releases to water

- Sodium hydroxide from water scrubbing of vented nitrogen and washing of equipment

Releases to land

- None.

2.1.8.4 Nickel catalyst manufacture

2.1.8.4.1 Typical catalyst manufacturing process

An aqueous nickel solution is prepared in a stirred vessel that is maintained under reduced pressure by a fan exhausting through a water-scrubber to atmosphere, by mixing ammonia solution, and nickel and ammonium salts. Extruded alumina is dried in an indirect gas-fired heater and then treated with the prepared nickel solution to impregnate the alumina with nickel ions, any ammonia liberated in the reaction being absorbed in a wet scrubber. Excess nickel solution is removed from the alumina support by vacuum filtration and recycled for the next batch. The resultant solid is hot-air dried and then subject to the requisite heat treatment. The catalyst product is classified to give the required product agglomerate size, and any oversize or undersize material that cannot be recycled within the process is sent for off-site recovery of the nickel.

Aqueous waste streams and spent scrubber liquors are passed through a sand filter to remove solid nickel particles, followed by an ion exchange unit to remove dissolved nickel ions. The ion exchange resin is regenerated with sulphuric acid.

2.1.8.4.2 Potential release routes from nickel catalyst manufacture

Releases to air

- Ammonia from wet scrubbers.
- Particulates from bag filters.

Releases to water

- Ammonia and nickel after filtration and ion exchange.

Releases to land

- Spent (i.e. un-regenerable) ion exchange resin, bag filter material and out-of-spec product.

2.1.8.5 Biochemical processes using ammonia

2.1.8.5.1 Biochemical ammonia-using processes

There are number of biochemical processes which use ammonia, ranging from plastic manufacture to human food production, but always with the same underlying principle of using ammonia both as a feed for the micro-organisms and to control pH. Typically, the micro-organism is dispersed in a deep fermentation vessel in an aqueous solution containing trace elements, and is fed with a carbohydrate, air and ammonia gas. When the processes have progressed far enough, the mixture is withdrawn, heated to stop further enzymic reaction and the product filtered off. The filtrate is discharged to an appropriate effluent treatment plant.

In many of these processes, due to the low steady temperatures and the pressure/depth conditions in the reactor, ammonia injected at the bottom is totally absorbed and a vent scrubber is not required.

2.1.8.5.2 Potential release routes from biochemical processes using ammonia

Releases to air

- Ammonia from vents.

Releases to water

- Filtrate containing ammonia/ ammonium and a high BOD

Releases to land

- None.

2.1.8.6 Ammonium salts manufacture

Ammonium nitrate manufacture is covered in Section on Fertilizers (**Section 2.1.10.1**). Other ammonium salts are as follows:

2.1.8.6.1 Ammonium carbonate/bicarbonate manufacture

These are considered together, as both involve the reaction of carbon dioxide with ammonia. Furthermore, liquor from the ammonium bicarbonate process can be used as raw material in the ammonium carbonate process.

For ammonium bicarbonate production, a near-100% carbon dioxide gas stream (usually vaporised from liquid CO_2) is absorbed in ammonium hydroxide solution. Typically, three ammonium-hydroxide-containing absorbers are used in series, with the first product slurry emerging from the first and the second and third absorbers maximising carbon dioxide utilisation. The ammonium bicarbonate slurry is thickened in a hydrocyclone before being centrifuged, separated and dried. The product is ground and then bagged. Air from the drying stage and extracted air from the grinding operation is filtered before discharge to atmosphere.

Commercial ammonium carbonate, which is a mixture of ammonium carbonate and ammonium bicarbonate, is produced by reacting ammonia gas and carbon dioxide in the presence of steam. The hot raw material gases are ducted to a number of condensers arranged in parallel, and condensation continues until the thickness of the product reduces heat transfer to the level where condensation ceases. At this stage the supply of feed gases to the condenser is stopped, the condensers opened and the ammonium carbonate removed physically for milling and packaging. At the start of the next cycle the condenser is purged with air to atmosphere.

Steam stripping of excess mother liquor from ammonium bicarbonate production provides a stream of ammonia and carbon dioxide which can be fed into the raw material feed stream for ammonium carbonate production. The residual liquor is discharged to drain.

2.1.8.6.2 Ammonium bisulphite/thiosulphate manufacture

Ammonium hydroxide is used for the manufacture of many ammonium salts, such as ammonium bisulphite and ammonium thiosulphate (and others such as ammonium bromide). In all these examples, whilst ammonia may be emitted there is also the potential for the release of acid gases.

Ammonium bisulphite is formed by reaction between aqueous ammonium hydroxide and sulphur dioxide, conducted continuously or in batch.

$NH_4OH + SO_2$ --------> NH_4HSO_3

The off-gases, containing ammonia and oxides of sulphur, pass to a water-irrigated mist eliminator where the ammonia (and some of the SO_2) is absorbed and returned to the process. The residual gas is treated in a sodium hydroxide tail-gas scrubber (which may also receive acidic off-gases from other sulphur dioxide absorption systems and be followed by an electrostatic precipitator or other high efficiency mist eliminator) or on a multi-product site may be used in other reactions that require sulphur dioxide. The ammonium bisulphite product liquor is polished, filtered and transferred to storage

Ammonium thiosulphate is formed by the reaction of ammonium bisulphite with sulphur and more aqueous ammonia:

$NH_4OH + NH_4HS0_3 + S$ -------> $(NH_4)_2S_2O_3 + H_2O$

The vent gases from the reactor are scrubbed with water and ammonium bisulphite (e.g. a venturi scrubber) and the liquor is returned to the reactor. After reaction the product is clarified and treated with active carbon. Periodically, solids containing metal sulphides and sulphur are bled off from the reactor to prevent build-up.

2.1.8.6.3 Ammonium phosphate manufacture

Mono-ammonium phosphate and di-ammonium phosphate are made by injecting gaseous ammonia into phosphoric acid (usually 50 - 55% P_2O_5) to produce a slurry of crystals of the respective products. The reaction is exothermic and requires water or other suitable recycle solution to act as diluent and control the temperature.

$NH_3 + H_3PO_4$ --------------> $NH_4H_2PO_4$

$2\ NH_3 + H_3PO_4$ -------------> $(NH_4)_2HPO_4$

The off-gases pass to a phosphoric acid scrubber which absorbs excess ammonia for return to the reactor. Where the product is not destined for the fertilizer market, the slurry is centrifuged to separate the ammonium phosphate, which is then dried and packaged for sale. The filtrate is returned to the reactor, though a bleed is taken off the recycle to prevent a build-up of impurities and this is sold into the fertilizer market. Where the product is for the fertilizer market, the slurry from the reactor is often fed directly to a granulator with, depending on the formulation of the final product fertilizer, sulphuric acid or other constituents being added before granulation.

Ammonium polyphosphate is produced by reacting pyrophosphoric acid with urea in a heated mixer. The off-gases are cooled by dilution with air and pass to a water scrubber, followed by a phosphoric acid scrubber. The product is milled and sized prior to packaging, Potential release points in the sizing and handling systems are protected by a bag filter unit.

Fluoride can be present in the phosphoric acid used in the phosphoric acid scrubbers, and it may be stripped from the acid in the scrubber and released to air, mostly as hydrogen fluoride. If food-grade phosphoric acid is being used, the HF release is insignificant.

2.1.8.6.4 Potential releases from ammonium salts manufacture

Releases to air

- Ammonia from vents and absorbers.

- Carbon dioxide, oxides of sulphur, hydrogen fluoride and other acid gases from absorbers.
- Ammonium salts in particulate form from dryers, solids handling, and milling operations.
- Ammonia, carbon dioxide, ammonium bicarbonate and ammonium carbamate during start of condensers in ammonium carbonate production.
- Ammonia from vapour pressure of ammonia above some salts such as ammonium carbonate. (Releases can also occur during digging out of condensers and milling of product.)

Releases to water

- Mother liquor from ammonium bicarbonate process containing ammonia.
- Process liquors from scrubbers that may contain ammonia, ammonium sulphite, ammonium sulphate or other salts.

Releases to land

- Solids and activated carbon from polishing filters on ammonium bisulphite and thiosulphite production.
- Metal sulphides and sulphur from filtration of ammonium thiosulphate liquors.

2.1.8.7 Manufacture of EDTA and related chelating compounds

2.1.8.7.1 EDTA production

The sodium salts of ethylenediamine tetra-acetic acid (EDTA) and other related chelating agents are produced by the reaction of ethylenediamine, or related compounds, with sodium cyanide, water and formaldehyde in stainless steel vessels:

$C_2H_4(NH_2)_2 + 4\ HCHO + 4\ NaCN + 4\ H_2O \text{ ---> } (NaOOC.CH_2)_2NCH_2CH_2N(CH_2COONa)_2 + 4\ NH_3$

Ammonia is released as a by-product of the reaction and boils off continuously. The ammonia is captured by condensation and/ or multi-stage scrubbers using cooled recirculated water as the scrubbing medium. Approximately 180 kg of ammonia is recovered, for sale as aqueous ammonia solution, per tonne of EDTA produced.

Same of the ammonia is cyanomethylated to form salts of nitrilotriacetic acid (NTA) and other related compounds, and these side-products remain in the product unless the free EDTA is precipitated by acidification.

An alternative commercial process - the Singer synthesis - involves reaction of hydrogen cyanide, formaldehyde and ethylenediamine to form insoluble ethylenedinitrilo tetraacetonitrile, followed by hydrolysis with sodium hydroxide to EDTA

To produce the acids from the sodium salts of the chelating agents, the solutions are treated with sulphuric acid or hydrochloric acid. The precipitated solid, e.g. EDTA itself, is separated by centrifugation and the filtrate, and any washings, are neutralised before discharge to liquid effluent.

2.1.8.7.2 Potential releases from the manufacture of chelating agents

Releases to air

- Ammonia from scrubbers.
- Ammonia, amines and formaldehyde from storage tank vents.

Releases to water

- Ammonia and possibly amines and formaldehyde from scrubber liquors.
- Filtrate from production of the acid form of the chelates, containing sodium sulphate, sodium chloride, chelating agents and, potentially, traces of amines, formaldehyde and cyanide.

As chelating agents are capable of mobilising and maintaining metals in solution and some, like EDTA, are not readily biodegradable, the fate of aqueous discharges containing chelating agents needs to be carefully assessed and appropriate pre-treatment undertaken.

Releases to land

- None.

2.1.8.8 Zeolite manufacture

2.1.8.8.1 Zeolite production

Solutions of sodium aluminate, sodium silicate, aluminium sulphate, and sodium hydroxide are mixed together in the right proportions, and soda-Y zeolite precipitates out. The solid zeolite is recovered as a slurry from a filter, the filtrate being recycled within the process, and is then washed and filtered again.

The soda-Y zeolite is washed with ammonium sulphate solution. This stage brings about an ion exchange between ammonium and sodium ions. The filter cake is water-washed to remove sodium sulphate and any excess ammonium sulphate.

The wet Y zeolite filter cake is dried in a gas-fired dryer and then converted to the final product in a gas-fired calciner. The vent streams containing combustion gases, ammonia and ammonia oxidation products pass to atmosphere via a bag filter and other abatement as appropriate.

2.1.8.8.2 Potential releases from zeolite production

Releases to air

- Ammonia and particulates from the calciner, dryer vent, product and ammonia storage.

Releases to water

- Any of the salts in the mix are potential pollutants but the main components are ammonium, sodium and sulphate ions.

Releases to land

- Off-spec zeolite material and general solid waste.

2.1.9 Sodium carbonate and bicarbonate manufacture

2.1.9.1 The Ammonia-soda (Solvay) process

The Solvay process consists of four main parts:

- Hydrated lime (calcium hydroxide) production;
- Wet processing section (in which sodium bicarbonate is produced from brine);
- Dry processing section in (which sodium carbonate is produced from sodium bicarbonate);
- Boiler house (for steam production).

The calcium hydroxide stage is covered in more detail in the Cement & Lime sector IPPC Guidance Note S3.01(**Ref 23**) and BREF (**Ref 1**),and the last stage will be covered in the Large Combustion Plant IPPC Guidance Note - but in the meantime refer to the equivalent IPC Technical Guidance Note (**Ref 21**)and the draft BREF (**Ref 1**). The following section briefly covers the first three stages and a flowchart of the process is shown in **Figure 2.20**.

The process uses ammonia and carbon dioxide to convert sodium chloride into sodium carbonate. There is a substantial amount of recycling of both gases, but particularly of ammonia.

The basic reactions are:

(1) $NaCl + NH_3 + CO_2 + H_2O$ ----------> $NaHCO_3 + NH_4Cl$

(2) $2\ NaHCO_3$ -------------> $Na_2CO_3 + CO_2 + H_2O$

Subsidiary reactions are:

(3) $CaC0_3$ ----------> $CaO + CO_2$

(4) $CaO + H_2O$ --------> $Ca(OH)_2$

(5) $Ca(OH)_2 + 2\ NH_4C1$ ----------> $2\ NH_3 + CaCl_2 + 2\ H_2O$

The carbon dioxide and ammonia liberated in equations (2), (3) and (5) are collected and recycled to the initial reaction. - and, theoretically, all the ammonia used is regenerated and recycled, but in practice there are losses, which are replaced with ammonia make-up. Historically, the make-up ammonia always contained hydrogen sulphide, which helps to prevent plant corrosion. If the imported ammonia has insufficient hydrogen sulphide, then sodium hydrogen sulphide is introduced.

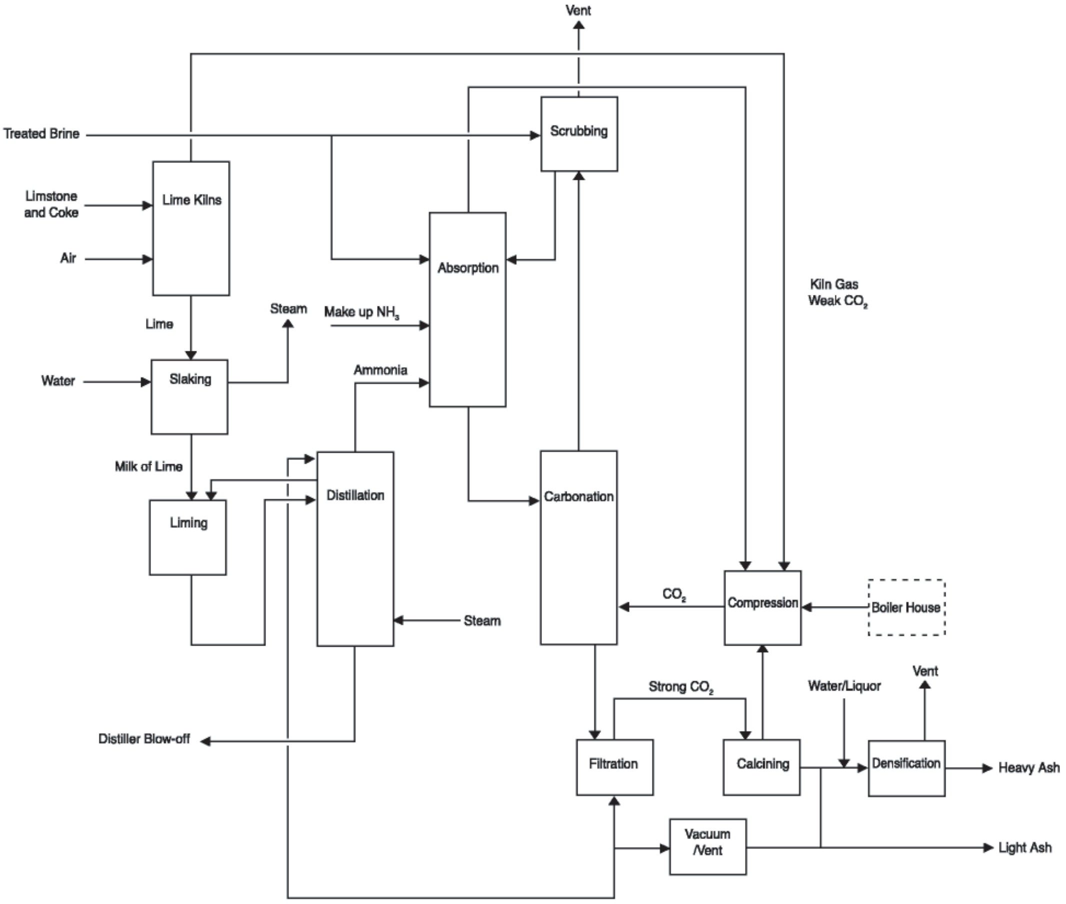


Figure 2.20: The Solvay ammonia - soda process

The carbon dioxide needed in the process comes from the burning of limestone in shaft kilns using coke as the fuel. Carbon dioxide is generated both from the limestone and from oxidation of the coke and the stream passes directly to the CO_2 compressors for feeding into the carbonation section of the process. Up to 10% of the stream may be bled-off to air for control purposes, though some of this loss may be reduced by use for carbonation of the distiller bottom off-take liquor. The calcium oxide product is hydrated in a rotary slaking plant to produce a calcium hydroxide slurry for use in the reclamation of ammonia.

Sodium chloride solution, which is supplied purified, is fed into the system through tower washers, which scrub various vents to remove and recover ammonia, hydrogen sulphide and some carbon dioxide from the main emissions from the process. Some of the brine is also used for scrubbing other vents.

The sodium chloride solution is fed to towers which absorber ammonia from the ammonia-rich gases that have arisen from distillation of limed ammonium chloride liquor which was the filtrate after separation of the crystallised intermediate product (sodium bicarbonate). Ammonia absorption is an exothermic reaction so the absorber liquor is removed part-way through the process, cooled and then returned to the absorber. The final liquor is cooled and stored in intermediate vats as "strong vat liquor" (SVL) before being passed to the carbonation stage.

Multiple towers are provided for carbonation and they are used alternately on a making and a cleaning cycle. In the cleaning cycle, the SVL is passes down counter-current to lime kiln gas (weak CO_2), and the agitation caused by bubbling the gas into the brine dissolves sodium bicarbonate scale deposited during the making cycle. The partially carbonated SVL then passes through a degasser and is pumped into the making tower.

The partially carbonated SVL enters the top of the making tower and on its passage down through the trays encounters carbon dioxide being fed into the tower in two places: half-way down - lime kiln gas, and at the bottom - mixed carbon dioxide, comprising lime kiln gas and the strong gas resulting from the calcination of the sodium bicarbonate. The tower is cooled internally to maximise the absorption of carbon dioxide and the precipitation/crystallisation of the least soluble species present, sodium bicarbonate:

$Na^+ + Cl^- + NH_4^+ + OH^- + CO_2$ ----------> $NaHCO_3 + NH_4^+ + Cl^-$

The precipitated sodium bicarbonate is vacuum-filtered from the liquor, rinsed and fed to steam-heated calciners ('light ash secheurs') where it is transformed to sodium carbonate .

$2\ NaHCO_3$ ------------> $Na_2CO_3 + CO_2 + H_2O$

The 'strong gas' so generated is cooled to condense out the water (which is recycled to the filter cake rinse stage) and, after scrubbing with incoming sodium chloride solution, is returned to the bottom of the carbonation making tower.

The filtrate from the bicarbonate filters contains ammonium chloride, ammonia and carbon dioxide, and pumped to the distillation section where ammonia and carbon dioxide are stripped out in the top section of the column. Further down, the liquors are mixed with calcium hydroxide (milk of lime) to liberate ammonia from the ammonium chloride. The ammonia is stripped out using live steam and both the ammonia and carbon dioxide pass to the absorber towers. The required small make-up of ammonia make-up is added to the distillers.

Solids in the distiller exit liquor are removed by settling and the residual liquor - in which calcium chloride is the main salt component - is neutralised with either acid or carbon dioxide. The final supernatant liquor is either discharged directly to water or, more frequently, following further settlement in lagoons (particularly, if carbonation has been undertaken) If settling lagoons follow carbonation, then the deposited solids are eventually disposed of to land.

The sodium carbonate made by this route is known as 'light ash', and it may be converted into denser 'heavy ash'. The light ash is hydrated with a sodium carbonate solution to produce the monohydrate, and then dehydrated by calcining in the 'heavy ash secheurs' to produce a pseudomorph of sodium carbonate. Particulate emissions from the 'secheurs' are controlled with dust arresters, which may be wet scrubbers.

All the products (light ash, heavy ash and purified sodium bicarbonate) are milled and screened before conveying to storage silos for final packing or loading into tanker lorries. All potential release points to air, such as screens, conveyors, silo exhausts, etc, are protected by bag filter units.

2.1.9.1.1 Potential release routes from the ammonia-soda process

Releases to air

- Ammonia, hydrogen sulphide and carbon dioxide from vents on absorbers, scrubbers and distillation units.
- Particulates from drying, storage and handling of product and wet particulates from the slaking of lime.
- Ammonia and hydrogen sulphide from vents on ammonia storage tanks.

- Hydrogen sulphide from vents on sodium hydrogen sulphide storage tanks.
- Carbon monoxide, oxides of nitrogen, oxides of sulphur, carbon dioxide and particulate matter from the lime kilns.

Releases to water

- Distiller bottom liquor containing chlorides, ammonia/ ammonium and possibly some phenols and cyanide content. Its composition is roughly 10% $CaCl_2$, 5% NaCl and ammonia/ ammonium amounting to 1-1.5 kg per tonne of product.
- Aqueous discharges from scrubbers and cooling water systems.

Releases to land

- Solids from clarification of distiller bottom liquor.
- General waste including contaminated product.

2.1.10 Fertilizer manufacture

The fertilizer manufacturing industry is a mature industry, and as a result of a variety of economic and financial pressures, has undergone dramatic restructuring in the last 30 years. All phosphoric acid manufacture has moved to the phoshate rock-producing areas and remaining UK nitrogenous and compound fertilizer plants are parts of foreign-owned international concerns. Apart from modifications to improve environmental and economic performance, much of the UK installed capacity is more than 20 years old.

Products manufactured in the UK include ammonium nitrate, ammonium phosphate, NPK fertilizers and single superphosphates through a variety of different processes. No urea-based fertilizers are currently produced but production of NPK blended fertilizers is reasonably buoyant as this only involves mechanical mixing which is a relatively low-cost technique.

A number of informative industry guides are available. These include a series of nine booklets on the production of various types of fertilizers and their pre-cursors (such as ammonia, sulphuric acid and nitric acid).

2.1.10.1 Ammonium nitrate production

2.1.10.1.1 Introduction

Commercial processes for the manufacture of ammonium nitrate (AN) usually involve the neutralisation of nitric acid by ammonia. On some plants the ammonia may be supplied as a liquid and vaporised using waste heat from the process.

Ammonium nitrate fertilizer plants typically produce a dry, free-flowing granular or prilled product from a concentrated solution of ammonium nitrate. There are many variations of details in the plants but there are three steps that are common to most:

- neutralisation of ammonia with medium concentration (50-70%) nitric acid, forming ammonium nitrate solution and steam;
- concentration of the ammonium nitrate solution by evaporation; and

- conversion of the solution or melt to solid particles with the properties and size range required by the market.

In some processes, the evaporation stage is eliminated as a separate step by using preheated ammonia and high-concentration nitric acid.

The following process description describes a typical neutralisation process with two-stage evaporation followed by prilling, and the corresponding flowchart is shown in **Figure 2.21**.

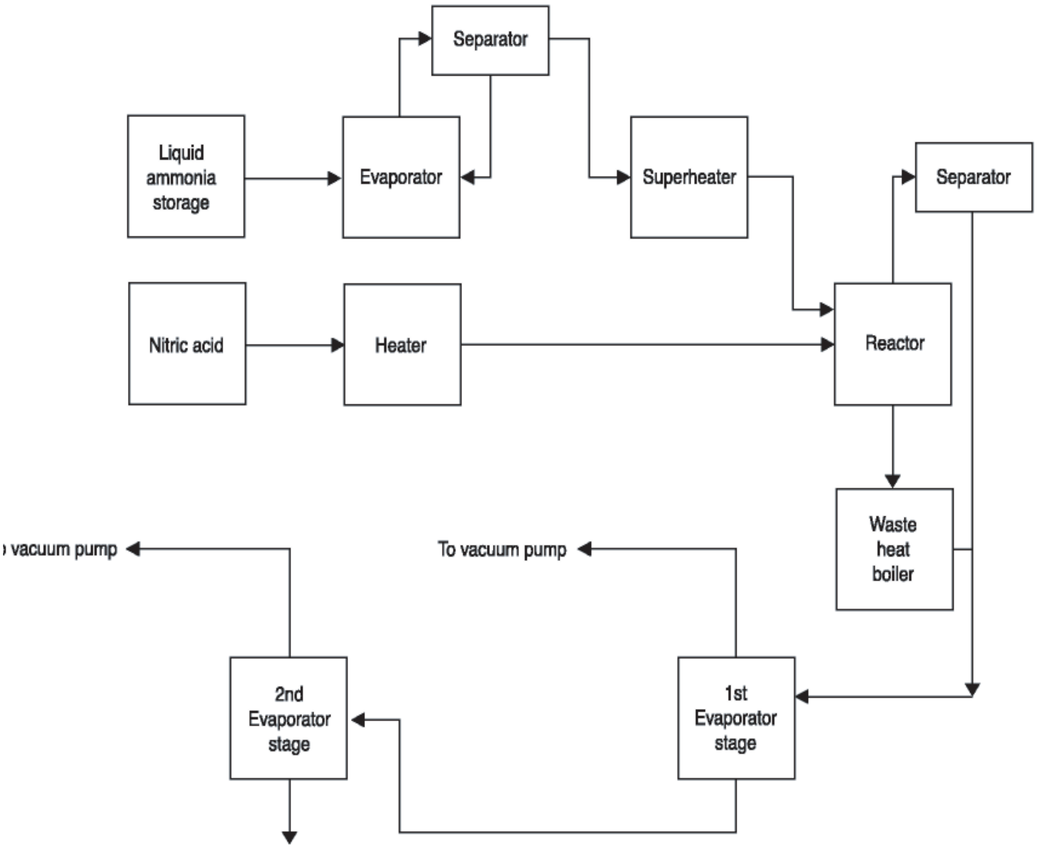


Figure 2.21: Manufacture of ammonium nitrate

2.1.10.1.2 Neutralisation of nitric acid with ammonia

The strongly exothermic reaction of ammonia with nitric acid to form ammonium nitrate is typically undertaken between 145 ºC and 185 ºC and at pressures up to 4.5 barg.

Ammonia, from either the evaporation of stored liquid ammonia or from an associated ammonia plant, is superheated and passed to the reactor where it reacts with pre-heated medium-concentration nitric acid. The nitric acid may be indirectly preheated by steam or hot condensate from the ammonium nitrate process. This neutralisation typically forms a 75-85% solution of ammonium nitrate:

NH_3 (g) + HNO_3 (1) -----------> NH_4NO_3 (l)

Since both reactants are volatile at the reaction temperature, conditions must be controlled to minimise the loss of materials. An excess of nitric acid, which is the less volatile of the two reactants, is maintained through most of the neutralisation but as ammonium nitrate becomes less stable as the pH falls below 4.5 it is important that as its concentration increases the bulk pH is not allowed to fall below this level.

The neutralisation reaction may be carried out in one or two stages. When a single reactor is used the pH of the reaction mixture is typically controlled between 5.0 and 5.5, and when two reactors are used the first stage is operated at a pH in the range 1 to 3 whilst alkaline conditions are maintained in the second stage. The use of two reactors generally results in lower overall emissions of ammonia as most boil-off steam is generated in the first stages of reaction and most ammonia emission towards the end.

A typical single reactor consists of a reaction chamber followed by an overhead vapour-liquid separator to disengage steam from the ammonium nitrate solution, a proportion of which is recycled to the inlet of the reactor. Nitric acid is mixed with the recycled AN solution via a sparge pipe in the inlet to the reactor and ammonia is injected in the base of the reactor and into the upward flow of solution via a separate sparge pipe. The reaction releases heat and generates steam which forces the solution up into the separator. From the separator, ammonium nitrate solution overflows to the next process, either a second reactor or the evaporation system, with a major fraction being recycled to the (1st) reactor inlet.

The temperature of the AN solution can be controlled by a combination of live steam production and indirect steam production in boiler installed in the reactor recycle circuit, by addition of contaminated condensate from the evaporators, and by control of the composition and feed properties of the reactants. Neutralisation at an elevated pressure will generate steam at a higher pressure and temperature but produce ammonium nitrate at a lower concentration.

Steam that is generated by the neutralisation reaction contains ammonia (0.5-1%) and ammonium nitrate. Recovery of both may be achieved by scrubbing with acidified condensate, the captured ammonia and ammonium nitrate being recycled to the reactor. This steam can also be used as a heat supply for the evaporation stage when vacuum is also used. A proportion of the condensate may feed back to the reactor in those processes that rely on returned condensate for temperature control. Where a scrubber has been used it is possible to reprocess this condensate further as suitable boiler feed water.

Ammonia gas may contain small quantities of inerts such as hydrogen, nitrogen and methane, so in some processes it will be necessary to vent these from the neutralisation system at an appropriate point.

2.1.10.1.3 Evaporation of AN solution

The procedures for evaporation of the neutralised solution vary depending on the water content of the reactants and on the evaporation temperature - though two- stage evaporators, usually operating under vacuum, are in common use. Evaporation is always performed using steam, which can come from the ammonium nitrate process (neutraliser) itself or from a steam raising facility on the site.

The concentration of the ammonium nitrate solution obtained is dependent upon the number of evaporation stages, with a 95% concentration from single stage and >99% concentration from two-stage evaporation. The units are usually thermally efficient and can be accurately controlled, but the decomposition potential of ammonium nitrate requires that the second-stage unit be designed to retain only a small amount of the concentrated solution.

The concentrated solution of ammonium nitrate must be kept at elevated temperatures to keep it liquid - and as such is commonly called the "melt". Precautions must be exercised to avoid contamination of any of the AN solutions with organic or other sensitising materials as these will promote decomposition - so the mixing of recycled streams has to be undertaken with great care.

2.1.10.1.4 Ammonium nitrate solidification

As an important constituent of fertilizers, ammonium nitrate is required to be free-flowing with good storage properties - but as ammonium nitrate is highly hygroscopic and cakes readily, the solid product should be protected from moisture and treated to minimise caking

Various procedures have been practised over the years to produce ammonium nitrate particles suitable for the required applications but the most two common methods for solidification are prilling and granulation. Whichever techniques is used, this final processing stage is also the completion of the evaporation stage.

(a) Prilling

From the evaporation stage the concentrated solution of ammonium nitrate is pumped to the top of the prilling tower, which is a tall empty tower with an upward flow of air. Droplets formed by the break-up of the liquid flowing from the distributor head, cool and solidify as they fall to the bottom and the air is discharged from the top of the tower via high efficiency filters that remove ammonium nitrate fume and dust. The free-fall height that is required to solidify the prills depends on the concentration of the ammonium nitrate, the prill diameter required, and the air velocity.

After the prills reach the bottom of the tower they must be cooled further and this is usually achieved by the use of a fluidised-bed or a rotary cooler. The cooled prills are then screened to remove fines and small amounts of oversize and fines (which are sold separately or recycled through the process).

Additives and other ingredients can be incorporated into the ammonium nitrate prills. Calcium ammonium nitrate (CAN) is made by adding calcium carbonate or dolomite to the ammonium nitrate. A magnesium compound is frequently added to the AN solution prior to prilling as an anti-caking and stabilising agent, and a surface coating of a proprietary additive can applied after prilling to improve handling properties.

(b) Granulation

'Granulation' refers to techniques using processes such as agglomeration, accretion, or crushing to make a granular fertilizer. Typical granulators include rotary pans and fluidised beds. Early plants use the prilling process, but since the early 1970s some plants have been built with granulators. The granulation process has the flexibility to produce granules of any reasonable size with less potential for air pollution than prilling due to the much smaller volumes of air discharged.

In one process, named spherodizing, cool air (refrigerated in hot weather) passes through a rotary drum that is typically 3.5 - 4.5 m internal diameter and 14-18 m long, in which concentrated ammonium nitrate solution is sprayed onto a cascade of granules falling from specially designed flights. The granule size is built up in successive layers to produce well-rounded granules. After screening, the granules are further cooled in rotary or fluidised-bed coolers and may then can be coated with a surface conditioner if required.

In another process, the granular product is formed by spraying concentrated AN solution on to a fluidised bed of recycled granules. Evaporation takes place and the size of granules increases. The resulting granules are screened and those within range are removed as product and cooled, with smaller granules being recycled to the fluidised bed and oversize material being crushed and added to the recycle stream.

2.1.10.1.5 Potential releases from ammonium nitrate production

Releases to air

- Gaseous ammonia and nitric acid/oxides of nitrogen from storage (vents and pressure relief devices).
- Particulates and ammonia from the reactor (neutraliser), cooler, dryers, other process vessels and material handling.
- Ammonia from reactor inerts purge.
- Ammonia from evaporator blow-down.
- Ammonium nitrate and ammonia from the prilling or granulation operations.

Releases to water

- Condensate effluent containing up to 1% ammonia and up to 1% ammonium nitrate from reactor (neutraliser).
- Ammonium nitrate and nitric acid from plant wash-down.

Releases to land

- None.

2.1.10.1.6 Control of releases from ammonium nitrate production

(a) Control of aqueous effluent

The main requirement is to reduce levels of ammoniacal nitrogen in the final effluent. Apart from internal recovery of ammonium nitrate and ammonia (e.g. scrubber liquor from the granulation plant air cleaning section being recycled through the further evaporation stages on the granulation plant), it is likely that on integrated fertilizer sites there will be possibilities for other site operations to use the liquid effluent streams from both the liquid AN and granular AN sections. For example, integration of these plants with nitric acid production can offer significant opportunities for achieving very low levels of liquid effluent from AN production.

Within the plant, steam contaminated with ammonia or ammonium nitrate can be purified before or after condensation. Before condensation, steam can be cleaned by:

- droplet separation techniques, such as:
  - knitted mesh demister pads,
  - wave plate separators, or
  - fibre (e.g. PTFE) pad separators.
- scrubbing devices, such as:
  - packed columns,
  - venturi scrubbers, or
  - irrigated sieve plates.

(Scrubbing devices normally employ nitric acid to neutralise any free ammonia and assist in the removal of the fine ammonium nitrate particles, but scrubbing with dilute ammonium nitrate solution followed by suitable demisting may also be employed.)

For purification of condensate techniques include:

- stripping with air or steam with the addition of alkali to liberate ionised ammonia if required;
- ion exchange;
- distillation; or
- membrane separation processes.

The choice of technique will depend upon whether nitrate removal is required and this will depend upon the receiving water.

Where effluent treatment involving distillation is employed, caustic soda is first added to the condensate to release ammonia from the ammonium nitrate. The first distillation column strips the ammonium compounds from the condensate and the stripped condensate containing <50 ppm ammoniacal N (5-10 ppm has been reported) forms the final effluent from the process. The top product, which is steam containing 10-12% of ammonia, passes on to a second column where ammonia is recovered as a 100% vapour for re-use in the main ammonium nitrate process. The total flow of effluent corresponds to the water that is entering with the nitric acid.

Aqueous wastes may contain nitric acid, nitrates and particulate matter as well as ammonia and nitric acid as well as particulate matter so may be acidic or alkaline and have to be neutralised accordingly.

(b) Control of ammonium nitrate fume, particulates and dust

Most of the air pollution from an ammonium nitrate plant is derived from the AN particulates and vapour that arise from prill towers or granulators. Most of the ammonium nitrate in the exhaust is in the form of very fine (sub-micron) particulate fume which, at concentrations around 15 mg/m^3, becomes visible as a persistent blue haze after the steam plume has dispersed. Conventional scrubbers are not very effective for the removal of particulates < 1micron; the most effective technique for the abatement of AN fume is the use of irrigated candle filters (usually with candles of very fine glass fibre) - but the cost does represent a significant proportion of the total plant cost.

A candle filter installation specified to handle all of a prill tower's exhaust gas is a very large and expensive item. For example, the gas flowrate associated with a 1700 tpd AN plant is about 500,000 m^3/hour and the cost of the air pollution control plant is in the range £5-10 million - and periodic replacement of the candle packing will cost tens of thousands of pounds.

The choice of the fibre in the candle filter is very important. Glass fibre is normally used but it requires tight pH control since it is attacked by both acid and ammonia. Ammoniacal conditions cause etching whilst acid conditions tend to cause breakdown of the sodium silicate bond so, typically, glass candle filters have a life of just 3-5 years. Organic materials might provide an alternative but they should only be used on AN duty after a detailed hazard study has established the safety of the application.

Acidic solution at around pH 2 is circulated over the filters until it reaches a 40% ammonium nitrate solution. This is then be mixed with off-specification AN from the prilling process to give a 60% solution, neutralised with ammonia and recycled to the neutralisation reactor. As with the handling of all AN solutions, pumps must not be allowed to become dead-headed as they could explode.

Cyclones and mesh filters may be employed upstream of the candle filters to remove particulates. The mesh filter is washed with up to 40% ammonium nitrate solution acidified with nitric acid to pH 2 - and at ambient conditions ammonium nitrate is stable at this concentration.

Some designs of prill tower use an internal shroud fitted around the spray distributor head to collect and treat the fume generated from the spray process. Air extracted from within this shroud contains AN particulates concentrations of 200-400 mg/ m^3 whereas that from outside the shroud is typically 50-60 mg/ m^3. High-efficiency collectors for the dustier stream can be sized for a smaller flow than for the same process operating without a shroud.

Although the nature of effluent generated in granulation plants is comparable to that generated from prill towers, the quantity of air to be treated is much smaller with a corresponding impact on abatement equipment size and cost. Depending upon the moisture content of the feed to the granulator, the subsequent emission may contain coarser particles and this generally allows use of cheaper abatement technologies.

Gases from the granulator (if applicable) and from the dryer may be cleaned by a combination of dry cyclones and wet scrubbers - including mesh or candle filters, venturi scrubbers and cyclones. However, candle filters are not suitable for control of larger particulates where calcium ammonium nitrate or other insoluble materials are added to the ammonium nitrate as these will rapidly foul the surface of the filter.

Techniques employed for cleaning air from prill towers and granulators may also be employed on coolers. Air from the outlet of the fluidised-bed coolers, cleaned typically by cyclones, can be mixed with the cleaned air from the candle filters to reduce plume visibility and to provide some buoyancy.

(c) Storage and handling of ammonium nitrate solution

Following primary production, the liquid ammonium nitrate may be pumped into heated intermediate storage tanks where it is kept in liquid form. Heat is usually provided by the use of an external heat exchanger through which the AN is recirculated. Steam coils should not be used in AN storage in case there is solidification and subsequent re-application of steam might cause detonation. Ammonia gas may be injected into the recirculating melt to maintain the ammonium nitrate at a stable pH and inhibit decomposition.

(d) Storage and handling of ammonium nitrate prills and granules

AN prills and granules are generally reasonably dust-free and screened product can be conveyed and elevated into storage facilities, but fugitive dust emissions will have to be controlled during conveyance and bagging of the product.

2.1.10.2 Ammonium phosphate fertilizer production

See ammonium phosphate manufacture in **Section 2.1.8.6.3** and NPK granulation in **Section 2.1.10.3.1**.

2.1.10.3 Manufacture of NPK fertilizers

The basic plant nutrients found in chemical fertilizers are nitrogen (N), phosphorus (P - stated as P_2O_5), and potassium (K - stated as K_2O). The product name is usually followed by three numbers that indicate the relative percentages of N, P_2O_5, and K_2O, the typical content of nutrients normally totalling between 40% and 60%. Typical sources of these constituents are ammonium nitrate, ammonium phosphate and potassium chloride respectively.

There are many processes for making compound or complex fertilizers and there are very large number of N/ P/ K ratios manufactured - but most of the processes are not carried out in this country. One such process is the nitric acid route or nitrophosphate process in which nitrate-containing straight and compound fertilizers are produced directly from rock phosphate, using all the nutrient components in an integrated process with no solid wastes and minimal gaseous and liquid emissions.

Processes covered in this Note include the ammonium phosphate/ ammonium nitrate route, and the mechanical blending of single or multi-nutrient components.

The preferred form of a solid fertilizer is a free-flowing, dust-free product and compound fertilizers are produced in two forms, either as granular or as blended product. Thus:

- A uniform granular compound fertilizer is manufactured by mixing solid and/ or liquid raw materials, some of which may react, to produce a granular product. The following feed materials are commonly used in the manufacture of NPK fertilizers: ammonium nitrate, ammonium phosphate, ammonium sulphate, urea, single super-phosphate, triple super-phosphate, potassium chloride, potassium sulphate. Each granule contains the N, P and plant nutrients at levels close to the declared values for the grade.
- A blended compound fertilizer is manufactured by simply mixing solid raw materials, and blended fertilizers are made without involving any chemical reaction. Blends do not necessarily consist of mixtures of straight fertilizers or single compounds; a blended compound fertilizer may comprise a blend of two or three uniform compound fertilizers.

2.1.10.3.1 NPK Granulation processes

The main chemical feeds for granulation can be produced on an adjacent plant, as often happens with ammonium nitrate, imported from other UK sites (e.g. ammonia) or imported from abroad (e.g. phosphoric acid or urea). Granulation plants are normally housed within buildings to maintain dry conditions for the raw materials and the bulk product, but after the final product has been bagged, it can be stored outside ready for shipment. A flowchart of a typical granulation process is shown in **Figure 2.22**.

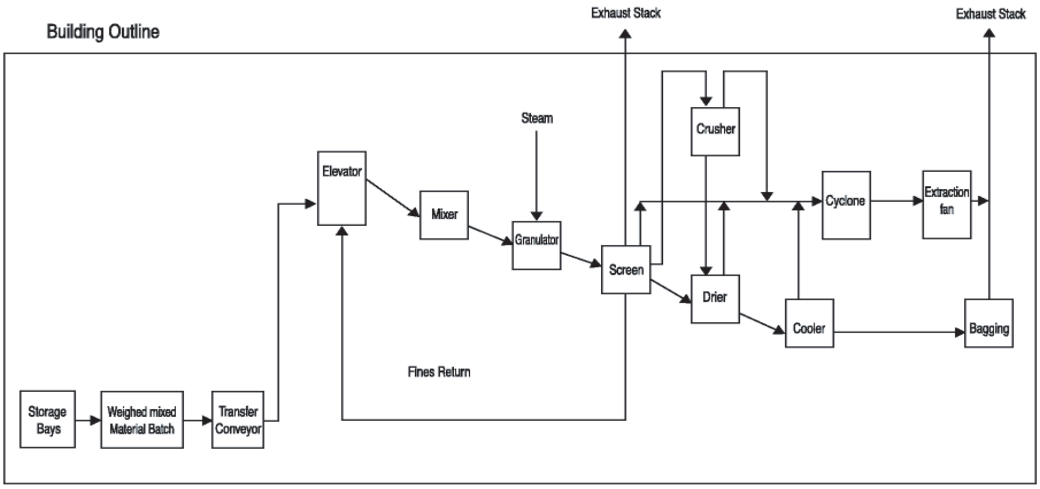


Figure 2.22: Typical granulation process

Granulation plants fall into two main categories, these being 'water-balance-limited plants' and 'granulation-limited plants' - but granulated product may also be made by a third method known as compaction granulation which is not described here.

(a) Water-balance-limited plants

In water-balance-limited plant, there is much more water associated with the raw materials than is required to form the solution phase for granulation - and these plants are sometimes called 'true granulation plants'.

A wide variety of raw materials may be used, depending upon the required fertilizer composition. The basic raw materials may include ammonium nitrate, phosphoric acid, potassium chloride, ammonia, potassium sulphate and/or super-phosphate, and there may also be secondary nutrients, micro-nutrients and filler.

Ammonia is reacted with phosphoric acid in a pipe-reactor to produce ammonium phosphate slurry which is fed forward to the granulation reactor. The ammonium phosphate reaction is exothermic and the temperature may be controlled by the introduction of recycled scrubber solutions.

The required solid raw materials (e.g. potassium chloride, and limestone filler) are commonly added to the recycle stream, upstream of the granulator or, alternatively, by mixing with the ammonium nitrate solution. They are conveyed from elevated storage silos and metered into the process. The slurry is fed at a controlled rate to the granulator, where it is mixed with ammonium nitrate solution and recycled solids (fines and crushed solids). The ammonium nitrate solution generally forms the bulk of the liquid phase required for granulation.

The tumbling action during granulation ensures the production of a homogeneous mix and aids the chemical reactions and granule growth. Wet granules from the granulator are discharged into a rotary co-current hot-air dryer (which can be as large as 30m long and 5m in diameter) from which the drying air passes to a wet scrubber to remove entrained product dust and traces of ammonia. Apart from the evaporation of excess water, the drying process also strengthens the granules against attrition during subsequent handling.

The granules leaves the dryer at about 90 ºC, and pass to vibrating screens. The screened product is then cooled to 40 ºC using air, after which the material is screened again to remove any fines formed in the cooler. Typical product granules are roughly spherical with diameters between 2 and 4 mm. Oversized granules are crushed and with the undersized material, are added to the recycle stream.

(b) Granulation-limited plant

In granulation-limited plant the water associated with the raw materials is less than is required to form a sufficient solution phase for granulation so a subsidiary supply of water, typically steam, is required. These plants are sometimes called 'mixer granulation plants', and in some of them the basic raw materials are all solids and there may be little or no chemical reaction involved.

Powdered materials are transferred by conveyor, elevator or screw feeder to a series of mild-steel rotating drums, the first of which may be used as a pre-mixer. The granulator plant can either be a rotary drum, where steam or hot water is injected, or a high-speed paddle-mixer, where only hot water is used. The wet granules are then transferred to a dryer that is typically a mild steel rotary drum fitted with lifters designed to drop the granules through a stream of hot air whose velocity is set to minimise entrainment and solids carry-over.

Downstream of the dryer the operations are similar to those in the water-balance-limited process outlined above.

Granulation finishing

The granules from either the water-balance- or granulation-limited processes are coated first with a suitable oil and then with a very fine coating of an anti-caking agent (such as talcum powder or kaolin) to enhance the storage and flow characteristics. Talc is more difficult to handle than clay and it has to be aerated to enable free flow. These coating agents are all in the range 1-10 micron in size.

The coating is applied by spraying the warm oil on to the rolling bed of the granules in the front section of the rotating drum to create a thin film of oil around each granule. Coating agent is then added via a screw conveyor part-way down the drum, which adheres to the oiled surface, with any excess being drawn off into a bag filter system and recycled to the feed hopper. The coated granulated product is then conveyed to the bagging section or the bulk storage area.

2.1.10.3.2 NPK Blending processes

Simple blending activities are often carried out by companies not involved in mainstream fertilizer production. The blending activities do not usually involve chemical reactions or granulation so they only become PPC-regulated if directly-associated with a listed activity.

NPK blending involves the physical mixing of dry powders or granules. The individual fertilizer materials, which may include micro-nutrients, are fed through a loading hopper into a mixer in which the materials are thoroughly mixed and then discharged. Conveying systems pass the blended product to the bagging section for packaging, though it is sometimes necessary to screen and/ or coat the blended material to ensure consistent quality. Incompatibility problems between some raw materials may lead to changes in the physical properties of blends, particularly in terms of solubility and hygroscopic properties.

Blending processes can be batch or continuous:

Liquid fertilizers

Some NPK fertilizers are solutions or suspensions of fertilizer materials in water, and they cover the range from single materials to complex mixtures of nutrients and trace elements. Chemical reaction on mixing is not usually significant - but there are exceptions such as the production of diammonium phosphate suspension or solution by the neutralisation of monoammonium phosphate or phosphoric acid with dilute (18%) aqueous ammonia.

2.1.10.3.3 Potential releases from NPK granulation or blending

Releases to air

- Ammonia emissions from the granulator, blender, dryer, etc.
- Particulate emissions of ammonium nitrate, ammonium phosphate or potassium chloride from the granulator, blender, dryer, etc. and large particulate (dust) from the cooler and dust abatement systems.
- Fugitive dust emissions from conveyors, screens and other solids handling equipment.
- Ammonium chloride or fluoride (ex-phosphoric acid) from the granulation plant.
- Visible saturated (steamy) plumes

Releases to water

- Wash-down waters and scrubber liquors.

Releases to land

- None.

2.1.10.3.4 Control of releases from NPK fertilizer manufacture

Sources of pollution on NPK fertilizer plants

The main sources of pollution on a compound fertilizer plant are the ammonia and particulates emissions from the granulator and dryer, and particulates from the product cooler. There are also fugitive dust emissions from the conveyors, screens and other solids handling equipment

There may be traces of fluorides in the stack gases arising from the use of phosphoric acid, and another potential source of pollution on NPK plants is the formation of a fine ammonium chloride fume.

Effect of particle size on particulate abatement plant design

An important parameter affecting the design and selection of suitable particulates abatement plant is the particle size and nature of the fume and particulates to be collected. The particulates in the exhaust gases from the granulator and the dryer are generally above 5 micron, with a little material between 3 and 5 micron in size.

The absence of very small particles allows satisfactory particulates removal using a low pressure-drop device (i.e. 150 to 350 mm water gauge) such as a wet cyclone.

Comparison of wet scrubbing and dry collection cleaning plants

The two main gas cleaning duties on a fertilizer plant (i.e. cleaning of granulator and dryer off-gases) usually require the use of wet scrubbing devices after primary treatment in cyclones because the off-gases contain water vapour and any condensation would seriously impair the operating effectiveness of bag filters or other dry cleaning equipment. Furthermore, apart from the solid particulates removal duty, there is also a requirement for ammonia and possibly fluoride absorption.

However, the use of wet scrubbers for all of the gas cleaning duties around the plant means that the plant water balance is affected. The bleed from the main scrubber can be returned to the granulator-reactor but any surplus of liquor from other scrubber systems has to be sold as liquid fertilizer or recovered or disposed of in another way.

Performance of wet scrubbers

Actual scrubbing efficiency depends on many factors but, in particular, it depends on particle size and pressure drop. In a wet scrubber the main running cost is the power required to overcome the gas-side pressure drop.

Table 2.3 illustrates the typical pressure drop and dust collection efficiency of several wet scrubbing devices used on fertilizer plants. The scrubbing liquor used in the wet scrubbers may be ammonium phosphate or ammonium sulpho-phosphate solution, the pH of which may be controlled by the addition of phosphoric and/ or sulphuric acid.

Table 2.3: Performance of wet scrubbers on fertilizer plants

Type	Pressure drop	Dust collection efficiency (%)		
	(mm wg)	1 micron	5 micron	10 micron
Simple void spray tower (Note (a))	50	40	94	96
Medium pressure drop scrubber	150-350	90	97	99
Venturi scrubber (Note (b))	600-1200	97	99.6	99.9

Note (a) - The performance of a spray tower passes into the second category if arrangements are made for spraying at several levels and using nozzles that give a good spray pattern.

Note (b) - Venturi scrubbers operating at lower pressure drops are available but the performance moves down to the second category.

General dusting abatement

For water balance reasons, the use of bag filters is generally preferred for general dust abatement duties such as the ventilation of conveyors and the other solids handling equipment. Because the dust loading tends to be high, the bag filter plant has to operate with a relatively low filtration velocity (< 1 m/ min) and low pressure drop (75-100 mm wg) - but this does extend bag life and improves the system reliability and integrity.

The typical face velocity for the collection of NPK dust is less than 1 m/ min and about 1.2 m/ min when collecting talc. The dust is usually hygroscopic and therefore the filters have to be heated to about 100C.

Fertilizer plant scrubbing

The main problem in a fertilizer plant scrubber is the practical one of plugging. Fertilizer dust tends to be sticky, and caking can occur if there is any build-up of solid in the equipment. This is why a tray type of unit (such as Peabody scrubber) would not be suitable.

Doyle scrubber

For many years the fertilizer industry has used the Doyle impingement scrubber in which the gases are passed through an annular section formed by the insertion of a cone in the bottom of a downcomer duct. This typically has a pressure drop of 150-200 mm wg and forces the dusty gas to impinge at high velocity on to the surface of a bath of liquid - the scrubber liquor typically containing up to 40% of dissolved solids. The disadvantage for granulator gas cleaning is that the gas has to pass through two units in series to ensure satisfactory dust removal. Furthermore, the Doyle scrubber cannot be regarded as an effective absorption device for gaseous contaminants; for example, when Doyle scrubbers are operated under acidic conditions, i.e. with the addition of phosphoric acid, there is a 'steamy' plume and emissions of hydrogen fluoride. There is also a tendency for blockages to occur.

Other scrubbers available are available which have more efficient gas-liquid contacting and are better at both absorption and dusting removal.

Airmix scrubber

The Airmix scrubber has been widely used in the industry. This is a self-induced spray-type device in which both the gas and scrubbing liquid enter the bottom of the unit at high velocity. As they decelerate in the diffuser section so that the liquid droplets tend to fall out of the gas stream and form a curtain of spray through which the gas stream passes and is scrubbed accordingly.

Granivore

This cyclonic spray unit, in which the liquid is introduced through the sides of the scrubber, also relies on vigorous scrubbing in a dense spray for effective operation. The location of spray nozzles across the gas stream is generally avoided because of the risk of plugging, erosion and corrosion.

Turbulent contact absorber

Static packed towers are not generally recommended for scrubbing gases laden with solids due to potential blockages. However, turbulent contact absorbers consisting of several beds of hollow propylene spheres that are 'fluidised' by the upward flow of dusty gas may be used - and the advantage of this scrubber is that it simultaneously absorbs and de-dusts.

Cyclones

Cyclones are generally employed as the main technique for dry particulate abatement in the manufacture of chemical fertilizers. They can be manufactured from a wide range of materials; and can be designed for high-temperature and high-pressure operation. Cyclones are suitable for separating particles down to about 5 micron thereby making them suitable for the exhaust air from granulators, coolers and dryers, and smaller particles down to about 0.5 micron can be separated where agglomeration occurs. High-efficiency cyclones are capable of removal efficiencies of the order of 90% for particles down to 5 micron but below this, collection efficiency drops off appreciably. High-rate gas cyclones have a removal efficiency of about 90% for particle sizes down to about 20 micron.

Stack exhausts

The main stack gases that are discharged to atmosphere from an NPK plant are saturated with water vapour at a temperature of about 35 ºC giving rise to a plume that is visible and steamy in appearance.

2.1.10.4 Single superphosphate manufacture

The production of single superphosphate (SSP) by a continuous process gives rise to particular difficulties in that the reactants, originally as a thin slurry, set to a solid mass during the reaction The equipment that overcomes this problem is known as a "superphosphate den" and the more common designs are the Broadfield den and the Maxwell den. The operating principles are essentially the same, with both producing solid superphosphate in a powder form by providing sufficient residence time for the SSP reaction to occur (though complete maturing of the product may take up to two weeks after initial production).

2.1.10.4.1 Chemistry of SSP production

Single superphosphate is made by the reaction of phosphate rock with sulphuric acid to convert the insoluble (tribasic) form of calcium phosphate to a soluble (monobasic) form. This reaction can be represented by the following chemical equation:

$[Ca_3(PO_4)_2]_3.CaF_2 + 7\ H_2SO_4 + 3\ H_2O$ ------> $3\ Ca(H_2PO_4)_2.H_2O + 7\ CaSO_4 + 2\ HF$

The calcium sulphate remains in the product and forms part of the fertilizer. SSP contains about 20% of phosphorus pentoxide (P_2O_5) equivalent, and in the past it used to be sold as 0-20-0 product.

The chemical impact of acid on phosphate rock liberates a large amount of steam, which entrains fine particulates of phosphate rock and acidic gas and fumes, most of which originate from impurities in the rock.

The evolution of fluoride-containing gases is a major problem in the SSP production process. These arise from the fluoride and silicon contained as impurities in the phosphate rock. These elements combine with the water to form fluorosilicic acid (H_2SiF_6). Any excess silicon dissolves (in acid) to form silicic acid ($SiO_2.H_2O$). Typical phosphate rock has about 8% silica (SiO_2) and 3%-4% fluorine by weight.

The temperature condition in the den causes a partial dissociation of fluorosilicic acid, according to the following chemical equation:

H_2SiF_6 <=====> $SiF_4 + 2\ HF$

Both SiF_4 and HF are gases at ambient temperatures and pressures and are collected by the den scrubbing system. Fluoride evolution varies between 10 and 50% of the fluoride in the rock, increasing with increased sulphuric acid concentration. SiF_4 hydrolyses to form silica that potentially could present maintenance problems within the scrubbing system so simple void spray towers and pigtail nozzles are preferred, often with once-through flow of scrubbing water.

During the curing process there are further fluoride losses, the amount depending upon the reaction time in the den.

The operation of a superphosphate den, once the correct ratio of acid and rock has been established, is entirely automatic, and only the minimum amount of attention is needed.

2.1.10.4.2 The Maxwell den

The shape of the Maxwell den is like that of a motorcar tyre that slowly rotates in a vertical plane. In place of the rubber tyre there is a cast-steel trough about 6 m in external diameter and 1.5 m in cross-sectional diameter. The reactor contains 12 tonnes of solid and at the typical output from a Maxwell den of about 3 tonnes per hour, the total residence time for the mixture to pass through the den is about three hours.

2.1.10.4.3 The Broadfield den

The Broadfield den is essentially a horizontal tunnel through which the slurry of acid and rock proceeds on a slowly moving slatted conveyor. Broadfield dens can be sized to handle 10 tonnes/hour and the residence time (which is determined by the speed of the conveyor) is typically around an hour.

2.1.10.4.4 Storage and maturing of SSP

The superphosphate material is then transferred from the den to storage piles where further curing takes place. It contains about 10% moisture and during this maturing stage the moisture content can reduce and the SSP can cake together. It is dug out with a mechanical shovel for further processing or for despatched in bulk or packaged form. As SSP is both an intermediate product used to make compound fertilizers and a horticultural fertilizer product, it is not usually necessary to complete the curing process (that would take ten days to two weeks).

2.1.10.4.5 Potential releases from single superphosphate production

Releases to air

- Plant emissions of hydrogen fluoride, sulphide and chloride, sulphur oxides, fluorosilicic acid mist and particulates.

Releases to water

- Weak acid effluent from scrubbers containing fluorosilicic acid and dissolved solids.
- Cadmium from phosphate rock, present in the weak acid effluent, and plant wash-down.
- Mercury from metallurgical sulphuric acid, present in the weak acid effluent, and plant wash- down.

Releases to land

- None.

2.1.10.4.6 Control of releases from SSP production

The main emissions from a single superphosphate (SSP) plant are the fluorine compounds and the particulates contained in the den exhaust gases. The normal method of gas cleaning is two-stage wet scrubbing.

Initial gas cleaning is achieved using one or more void spray towers arranged in series, operating with once-through scrubbing water to avoid the possible build-up of solids that could occur through silica deposition.

A high-efficiency scrubber is needed for the second stage, and a venturi scrubber with a pressure drop of 600 to 1000 mmwg can be used for this purpose. pH control can be effected through batch dosing with caustic soda.

Emission levels from a Maxwell den, before and after treatment in this way are illustrated in **Table 2.4**.

Table 2.4: Emission from a Maxwell den

	Inlet	Outlet
Sulphur dioxide, (mg/m^3)	300	40
Sulphur trioxide, (mg/m^3)	100	2
Fluorine compounds, (mg/m^3)	90	1
Particulate matter, (mg/m^3)	900	20

On a Maxwell den it is possible that, when starting with an empty plant, there may be a need for greater ventilation than is required when the den is operating normally. This is because in normal operation the den is sealed against air egress by the material contained within the den. If there is limited ventilation capacity then there is a possibility of dust puffing out into the working environment. Releases can be prevented by ensuring adequate hooding around potential leakage points or by providing enhanced ventilation from a stand-by fan for use at start-up.

2.1.11 Hydrogen cyanide manufacture

In the UK, hydrogen cyanide is both produced directly and sourced as a by-product from acrylonitrile production. In addition to its own direct use (e.g. in acetone cyanohydrin manufacture) it is widely used in the form of sodium cyanide for a diverse range of applications, including a wide range of applications in the metal finishing industry.

There are two main processes for the direct synthesis of hydrogen cyanide - the Andrussow process and the Degussa (BMA) process:

2.1.11.1 Andrussow process

The Andrussow process is the traditional route for producing first-intent hydrogen cyanide in the UK. The feedstock is a gaseous mixture of ammonia, air and natural gas which is passed over a platinum/ rhodium gauze at 1100 °C to give hydrogen cyanide, water and a significant quantity of impurities - though variations of the process use oxygen-enriched air or simply oxygen. The reaction is exothermic and heat is recovered as steam. The required reaction is:

$2\ NH_3 + 3\ O_2 + 2\ CH_4 \text{ ----------> } 2\ HCN + 6\ H_2O$

The separation and purification stages are:

- Absorption of unreacted ammonia and water into ammonium sulphate/ sulphuric acid solution, producing ammonium sulphate solution.
- Absorption of HCN from the gas stream in chilled water, with the tail gases passing to a burner for recovery of the calorific value of the stream.
- Stripping the hydrogen cyanide from solution and distillation to give pure product.

Distillation and stripping vents are fitted with refrigerated guard condensers to maximise recovery of hydrogen cyanide. To prevent polymerisation, small quantities of stabilisers (usually sulphur dioxide, phosphoric acid or acetic acid) are added to condensed hydrogen cyanide and to vapour spaces.

During start-up, feed gas passes to a diverter stack until the right conditions have been established to allow the gauze to be lit safely. As the catalyst gauze ages, the HCN yield from the main reaction falls progressively and a new gauze has to be fitted.

2.1.11.1.1 Potential releases from the Andrussow process

Releases to air

- Methane, ammonia, hydrogen cyanide, carbon monoxide and their combustion products, following passage through the tail-gas burner.
- Methane and ammonia during start-up.
- Hydrogen cyanide in very small quantities from plant ventilation systems.

Releases to water

- Various cyanide-containing liquors from the process, and washing liquors containing sulphuric and phosphoric acid, ammonium sulphate and sodium hypochlorite. (Cyanide-containing liquors are treated with hypochlorite under pH control to destroy the cyanide.)

Releases to land

- No planned releases to land. (Spent Pt-Rh catalyst is returned to the supplier for recovery.)

2.1.11.2 Degussa (BMA) process

In this process ammonia is reacted directly with natural gas, at elevated temperature in the presence of a platinum catalyst, in a heated tubular reactor, The Degussa process, which is endothermic and produces hydrogen as co-product, gives good yields of HCN without the side reaction products of other processes. However, these advantages are countered by the critical requirement for precise process conditions to prevention reactor damage. The economics of the process are likely to depend on the operator having a valuable use for the co-produced hydrogen.

$CH_4 + NH_3$ --------> $HCN + 3 H_2$

2.1.11.2.1 Potential releases from the Degussa (BMA) process

Releases to air, water and land

- The releases are similar to those from other HCN-producing processes.

2.1.11.3 BP Sohio process for acrylonitrile production

In this process, which is covered more fully in IPPC Technical Guidance Note S4.01 - Large Volume Organic Chemicals (**Ref 23**) and in the BREF of the same name (**Ref 1**), acrylonitrile is produced by the vapour-phase ammoxidation of propylene with ammonia and air in the presence of a heavy-metal catalyst. A significant quantity of by-product hydrogen cyanide is produced in this reaction, along with more minor quantities of other by-products.

The separation and purification stages consist of a series of absorption, stripping and distillation techniques to yield acrylonitrile and hydrogen cyanide products.

The hydrogen cyanide is generally used on site or piped to a third party, but can be burnt in a boiler for safety reasons if no demand exists or the onset of polymerisation is detected.

2.1.12 Use of hydrogen cyanide in manufacturing activities

Whilst the use of hydrogen cyanide in any manufacturing activity is listed for regulation as a Part A(1) activity within the PPC Regulations, the most significant uses are for the production of a number of inorganic and organic chemicals - and only these are covered below.

2.1.12.1 Sodium and potassium cyanide manufacture

NaCN and KCN can be produced batchwise or continuously, with hydrogen cyanide being added to a solution of the relevant hydroxide. Careful control of reaction conditions is necessary to prevent the formation of sodium formate by-product or free HCN in the product solution.

Depending upon the source of the hydrogen cyanide, further processing of the liquor may be required to remove carbonates and bicarbonates that can be present in the solution and where carried out this purification stage results in the production of a calcium carbonate/ bicarbonate-based waste slurry.

Solid sodium and potassium cyanides are produced by evaporating the above solutions and filtering the resultant slurry. Condensate from this evaporation can contain ammonia and hydrogen cyanide and so passes to effluent treatment. The solid cyanide product is extracted from the slurry using centrifuges, with the filtrate being returned to the evaporator. It is then dried and can be pressed to produce dust-free lumps. Granular material can be produced by coarse milling and screening of the lumps, any rejects from the screening process being recycled to the press. Any vents such as the dryer vent are water-scrubbed and any cyanide-containing liquor is returned to the process. Local area extraction systems to remove dusts from the workplace contain cyanide-contaminated material, and this should also be recovered where possible.

2.1.12.1.1 Potential releases from sodium/potassium cyanide manufacture

Releases to air

- Inorganic cyanides and hydrogen cyanide from process/ scrubber vents, dryer vents and plant ventilation systems. (Scrubber liquors should be recycled to the process.)

Releases to water

- Calcium carbonate slurry and various cyanide-containing liquors from the process and washing. The largest stream is the evaporator condensate.
- All cyanide-containing waste is treated with hypochlorite under controlled pH conditions to destroy the cyanide.

Releases to land

- Contaminated consumable items, e.g. damaged packaging, filter media, etc. Wherever possible, items are washed with water to decontaminate and the resultant liquor treated as a release to water.

2.1.12.2 Acetone cyanohydrin manufacture

Acetone cyanohydrin is an intermediate in the production of methyl methacrylate and methacrylic acid (see IPPC Technical Guidance Note S4.01 - Large Volume Organic Chemicals (**Ref 23**)), though other routes to methyl methacrylate not involving the use of hydrogen cyanide are also in commercial use. In the acetone cyanohydrin process the majority of acetone cyanohydrin is both produced and consumed on the same site.

Acetone is reacted with hydrogen cyanide in an exothermic base-catalysed reaction carried out in a reactor with pumped loop circulation to provide mixing. The reactants are fed under ratio control to optimise process conditions. Reaction conditions are carefully controlled and yield optimisation is achieved using successive cooling and holding steps. The reactor vent containing hydrogen cyanide passes to an acetone-irrigated scrubber and the resultant liquor is recycled to the process.

Impurities are removed by distillation to yield the product. In some arrangements the still may give a waste-side stream of water from the hydrogen cyanide reaction, which is contaminated with acetone and hydrogen cyanide. This stream passes to effluent treatment.

2.1.12.2.1 Potential releases from acetone cyanohydrin manufacture

Releases to air

- Acetone vapour and hydrogen cyanide from the scrubber or vacuum vents and from plant ventilation systems.

Releases to water

- Various cyanide-containing liquors from the process and plant washing. All such liquors are treated under pH control with hypochlorite to destroy the cyanide.

Releases to land

- There are no planned releases to land.

2.1.12.3 Cyanogen chloride manufacture

Cyanogen chloride is used as an intermediate in the manufacture of other chemicals (e.g. diphenylguanidine) and is usually generated as required. For ease of processing, a hydrogen cyanide solution is often generated in situ by the action of an inorganic acid on a solution of sodium cyanide. Chlorine gas is added under controlled conditions, generating cyanogen chloride gas, which is passed straight into the next process/reaction stage. The rate of cyanogen chloride evolution is controlled by the chlorine addition rate, and at the end of each batch or run, the reaction liquors are stripped to obtain all the available cyanogen chloride.

Owing to the toxic nature of both reactants and products, the reactor emergency relief systems vent to a total containment system.

2.1.12.3.1 Potential releases from cyanogen chloride manufacture

Releases to air

- Hydrogen cyanide, chlorine and cyanogen chloride from sodium hydroxide scrubber vents or plant ventilation systems.

Releases to water

- Various liquors possibly containing sulphate, chloride, cyanate, cyanide, cyanogen chloride and their respective hydrolysis products.
- Any cyanide-containing liquors are treated to remove cyanide using one of the methods indicated in in **Section 2.1.12.5.4** below and in the general section for general abatement methods, **Section 2.2.2**.

Releases to land

- There are no planned releases to land.

2.1.12.4 Manufacture of other hydrogen cyanide derivatives

Hydrogen cyanide generated from acidified sodium cyanide or hydrogen cyanide synthesised directly, can be used in the manufacture of a range of chelating agents, cyano-pigments, cyano-organic chemicals and intermediates for a range of organic chemicals. Most operations in this category are batch operations.

Whilst there are releases which are similar to those in the sections above, other potential releases will be specific to the derivative being produced.

2.1.12.5 Control measures for hydrogen cyanide

2.1.12.5.1 Storage and transportation of HCN

Hydrogen cyanide is classified as highly flammable so storage systems are often fitted with a water deluge system in case of fire. Any such fire water should be collected and treated before disposal.

When filling rail cars with hydrogen cyanide, the system should have movement sensing devices and all connections should be pressure-tested before use to aid prevention of accidental spillage and leakage. Systems should be provided with remote monitoring for leakage and remote means of isolating the rail cars from the hydrogen cyanide supply A Code of Practice (**Ref 26**) covers the storage and safe handling of hydrogen cyanide.

Hydrogen cyanide tends to polymerises, so to prevent polymer build-up in equipment such as pipework or rail cars, the equipment is routinely treated with dilute phosphoric acid. These washings should be retained for re-use but eventually they become exhausted and require disposal after treatment before.

2.1.12.5.2 Use and handling of hydrogen cyanide

Notwithstanding the industry Code of Practice of 1993, the following summarises the techniques likely to be encountered within plants using and handling hydrogen cyanide.

Hydrogen cyanide is a highly flammable liquid and can polymerise in the presence of heat, alkali and moisture. At concentrations between 3% and 90%, autocatalytic exothermic polymerisation can take place, which in an enclosed space can lead to explosion. To prevent such a situation, stabilisers are added to liquid hydrogen cyanide - the normal stabilisers being dilute phosphoric acid, sulphuric acid, acetic acid or sulphur dioxide. It is also common to have emergency dump systems containing stabiliser, situated above the storage tank.

Hydrogen cyanide boils at +26 ºC At temperatures above +5 ºC the vapour is above the upper explosive limit. The normal storage temperature is +1 ºC to keep the temperature (and vapour pressure) as low as possible, but sufficient to prevent the formation of ice on transfer lines being mistaken as leaks. At this temperature nitrogen purging is required on the storage tank. To prevent vapour loss it is preferable for the nitrogen to be added between the guard condenser and the absorber, unless the absorber liquors are recycled to the process, when the nitrogen purge can go direct to the storage tank.

Unstabilised hydrogen cyanide vapour can exist in head spaces, so polymer can build up in strategic areas (e.g. condensers). Most plants have systems for adding stabiliser to areas at risk, or for flushing with dilute phosphoric acid.

Hydrogen cyanide should not be stored for extended periods unless routine testing confirms the product quality. If pipework is not to be used for more than 72 hours, the hydrogen cyanide should be blown clear with an inert gas (usually nitrogen) to either storage or process, and the lines washed with dilute phosphoric acid (or other stabiliser), that is then retained for reuse wherever possible.

Stainless steel is the preferred material of construction. Pipework should be continuously welded wherever possible and indirect drive or canned motor pumps should be used. Inventories should be kept as low as reasonably practicable without causing operational problems, and storage tanks should be segregated from other chemicals by means of a dedicated bunding arrangement.

2.1.12.5.3 Control of hydrogen cyanide releases to air

There are several techniques applicable to the abatement of hydrogen cyanide in vent streams - including condensation, absorption (water or caustic solutions in ejector or scrubber systems), flaring and incineration. In the case of absorption systems, care must be taken when using alkaline absorbents to ensure that traces of alkali cannot reach systems containing liquid hydrogen cyanide owing to the potential hazard of runaway polymerisation.

Most processes involving hydrogen cyanide that generate particulate emissions (e.g. sodium cyanide manufacture) also require control of HCN at very low emission levels . Because of this, it is unlikely that electrostatic precipitation or dust filtration will be suitable.

2.1.12.5.4 Control of cyanide releases to water

Hydrogen cyanide or inorganic cyanide can be present in scrubber liquors, aqueous streams from stills, plant washing and other more minor sources. All such sources should be identified and the liquors treated prior to disposal.

There are several chemical processes for treating cyanides in water. The main methods currently in use are:

- oxidation with sodium hypochlorite to cyanate;
- oxidation with hydrogen peroxide to cyanate; and
- reaction with formaldehyde to hydrolysable cyanohydrin.

(a) Sodium hypochlorite treatment

The cyanide is oxidised to the cyanate by sodium hypochlorite at pH 10+ (at pH <10 cyanogen chloride and hydrogen cyanide may be formed). The reaction is as follows:

$NaOCl + NaCN + aq$ ---------> $NaCNO + NaCl + aq$

The reaction is rapid and the cyanate cannot readily be reduced back to cyanide - and cyanate is readily biodegradable.

The system lends itself to automatic control as completion can be monitored by measuring the electro-potential of the effluent. Excess hypochlorite has the potential to release chlorine whereas lack of hypochlorite leads to incomplete cyanide destruction so the final effluent should be continuously monitored for cyanide, chlorine and pH.

(b) Hydrogen peroxide treatment

Hydrogen peroxide can also be used to oxidise cyanide at around pH 9 to cyanate. It is more expensive than hypochlorite but it is easier to control and cannot release chlorine so is often favoured by batch manufacturers who deal with smaller effluent volumes but have high cyanide content in unreacted effluent.

(c) Formaldehyde treatment

At pH 8-14 formaldehyde oxidises cyanide to formaldehyde cyanohydrin, which in turn slowly hydrolyses in water to ammonia as given in the following equations:

$NaCN + HCHO + H_2O$ ------> $CH2OH.CN + NaOH$

$CH_2OH.CN + 2\ H_20$ --------> $CH_2OH.COOH + NH_3$

The process has the disadvantage that ammonia is formed, which can present an odour problem, and excess formaldehyde can be present in the effluent. However, all other products are easily biodegradable and the process readily goes to completion even in the presence of inhibitors (e.g. n-butanol). Formaldehyde treatment is usually only encountered in batch manufacturing operations where it is used to treat washes, etc, with very high cyanide concentrations and where it can be carried out in the reactor as the use of formaldehyde is the most volume-efficient of all the processes.

(d) Other methods for removing cyanide

The following alternatives can be used depending upon factors like volume and composition of the effluent:

- ion exchange;
- enzyme degradation;
- biological treatment (in conjunction with other wastes); and
- high-temperature incineration (high concentrations only).

2.1.13 Use of hydrogen sulphide in manufacturing activities

2.1.13.1 Production of Hydrogen sulphide

Hydrogen sulphide is not deliberately manufactured (other than in small quantities) but is a by-product in the manufacture of carbon disulphide and other, mainly organic, sulphur-containing compound. It is also produced as an intermediate in the de-sulphurisation of oil and gas. Sulphur recovery is covered below, but more information on these activities is available in IPPC Technical Guidance S4.01 - Large Volume Organic Chemicals (**Ref 23**) and in the Refinery BREF (**Ref 1**).

As well as being a by-product in some significant processes, hydrogen sulphide is released in smaller quantities from a wide range of PPC activities.

2.1.13.2 Manufacture of sodium sulphides

These reactions are usually carried out continuously in a packed tower, by reacting sodium hydroxide counter-currently with hydrogen sulphide. Stoichiometric amounts of sodium hydroxide (45-50 wt%) produce a solution of sodium hydrogen sulphide (NaHS liquor); excess sodium hydroxide produces sodium sulphide solution.

NaHS liquor is usually used without further treatment (other than dilution), whereas sodium sulphide solution is usually turned solid sodium sulphide flake.

2.1.13.2.1 Potential releases from the manufacture of sodium sulphides

Releases to air

- Owing to the low odour threshold, hydrogen sulphide from final process vents and final tanker filling vents is usually abated by a sodium hydroxide scrubber.

Releases to water and land

- There are no planned releases of prescribed substances to water or land.

2.1.13.3 Viscose processes

A number of different viscose products are manufactured either directly from wood pulp or from viscose solution itself. Just two are described below as all the processes have similarities and the releases from the processes differ only in detail.

2.1.13.3.1 Manufacture of viscose fibre

Wood pulp is mixed with dilute sodium hydroxide to produce a slurry in which the pulp fibres have separated and swollen. The slurry is de-watered using presses to form sodium alkali cellulose - and the sodium hydroxide solution that is separated is recycled back into the process.

The alkali cellulose is then oxidised by air permeation to reduce the cellulose polymer chain lengths to the required degree of polymerisation for subsequent processing. The oxidation stage may typically be carried out in bins, in silos, or on moving belts.

The oxidised cellulose is then reacted with carbon disulphide to produce sodium cellulose xanthate. This may take place as either a batch or a continuous process, but in both cases the reaction is carried out in the absence of air. At the end of the reaction, the remaining unreacted carbon disulphide is vented-off.

The cellulose xanthate is dissolved in dilute caustic soda either in the reaction vessel or in a separate tank to form the viscose solution and is passed through mechanical cutters/ attritors to aid dissolution.

This viscose solution is stored in tanks to age the viscose to the condition required for extrusion, and then filtered to remove inorganic particles and any undissolved wood pulp. It is then deaerated and pumped at a metered rate to a series of spinnerets (jets) and extruded through the holes in the spinneret into the spin bath. The spin bath contains a mixture of sulphuric acid, zinc sulphate and sodium sulphate - and, in contact with the spin bath mixture, the viscose is regenerated to cellulose with hydrogen sulphide and carbon disulphide formed as by-products. The freshly regenerated cellulose filaments are then collected together and stretched to align the cellulose molecules in the filaments.

The filaments may be processed in continuous form or cut into staple fibres, but in both cases, the fibre is passed through a series of washing and treatment stages to remove residual sulphur compounds, to neutralise the filaments fully, and to apply a processing lubricant. Finally, the fibre is dried prior to packaging.

2.1.13.3.2 Manufacture of cellophane

Xanthate solution is produced as described above for the manufacture of cellulose fibre. Film formation is achieved by 'pouring' this liquid through a narrow slot into a bath containing sulphuric acid and sodium sulphate. The film is then transported down a train of baths by a series of rollers and immersed tubes, the composition of the baths changing from highly acidic to alkaline. This process completes the reformation of the cellulose into a transparent film. After washing, the film is bleached and after further washing, is softened with a solution of glycerol and monopropylene glycol. It is then driven over a series of heated rollers in an oven and cut to size.

Various grades of film of differing permeability and semi-permeability are manufactured by incorporating anchoring agents in the last stage of wet processing, and applying aqueous- or solvent-based coatings to the dried film.

2.1.13.3.3 Potential releases from viscose processes

The following sections are relevant to most viscose processes.

Releases to air

- Waste process gases are likely to contain hydrogen sulphide and carbon disulphide and should, where practicable, undergo sulphur recovery.
- Contaminated extraction air can be dealt with most easily by incineration. Otherwise, activated carbon or biological filters may be considered.
- Amine, caustic scrubbing or other systems may be appropriate for particular releases.

Releases to water

- Effluents containing carbon disulphide, hydrogen sulphide, mercaptans or other organic sulphur compounds, may originate from scrubbing systems, process wastes and from routine cleaning of equipment -and are likely to require primary and secondary treatment prior to discharge.
- Spent scrubber liquors can be treated with hypochlorite to form inert chlorates of sulphur.
- Hypochlorite or other easily handled oxidant (such as hydrogen peroxide or ozone) should be considered for the elimination of odours in effluent.

Releases to land

- All solid wastes - process and spent consumables such as drums, sacks and rags - are likely to contain organic sulphur compounds. These compounds should be removed prior to landfilling or the wastes should be suitably contained to prevent release of the sulphur component.

2.1.13.4 Control measures for hydrogen sulphide

2.1.13.4.1 Handling of hydrogen sulphide

Hydrogen sulphide is highly toxic and flammable, with a characteristic smell of rotten eggs at low concentrations. (50% of the population can identify the smell at 1 mg/ m^3. At higher (toxic) concentrations or after prolonged exposure, the smell cannot be detected so the use of continuous monitors is essential.

Hydrogen sulphide is stored under pressure (usually at 25 barg) and the storage area may be protected by a water deluge system in the event of fire. Inventories of hydrogen sulphide should be kept as low as possible.

When hydrogen sulphide is dry, mild steel is an acceptable material of construction but if there is the potential for water or water vapour to be present, stress cracking is possible, so stainless steel or aluminium become the preferred materials of construction. To reduce the potential for fugitive releases, pipework should be continuously welded wherever possible and glandless or efficient seal systems used.

2.1.13.4.2 Control of hydrogen sulphide releases to air

Hydrogen sulphide should, as far as is practicable, be removed from waste gas streams prior to discharge to the atmosphere.

Absorption into sodium hydroxide is usually used in the inorganic chemical industry to remove hydrogen sulphide from vent streams but alternative abatement techniques include incineration and absorption into water, other neutralising agent, or low-vapour-pressure oil depending on the nature of other contaminants to be removed. Hydrogen sulphide and mercaptans are often released together and in conjunction with organic species, which may determine the choice of technique to be used.

Where a scrubber is used for odour control, the absorbent is often an oxidising reagent such as potassium permanganate or sodium hypochlorite. Newer technologies include the use of proprietary catalysts in conjunction with conventional hypochlorite scrubbing systems to enhance removal of the odours, and adsorption using an activated carbon system impregnated with potassium or sodium hydroxide.

Most processes involving hydrogen sulphide that generate particulate emissions also require control of H_2S at very low emission levels. Because of this, it is unlikely that electrostatic precipitation or dust filtration will be suitable.

Waste streams rich in hydrogen sulphide can be passed through sulphur recovery units for conversion to elemental sulphur, and these is covered below:

2.1.13.4.3 Sulphur recovery from H_2S gas streams

New sulphur recovery plants should use enhanced techniques such as super-Claus, or the equivalent. Tail gas treatments such as flue gas desulphurisation, or the SCOT process should also be considered where appropriate. Claus -type processes and alternative direct oxidation (redox) processes are described below.

Claus sulphur recovery

There are a number of Claus-type sulphur recovery techniques currently employed in other industries, and developments are continuing to improve them, and all follow an initial absorption stage, examples of which are:

- mono- and di-ethanolamine processes;
- hot carbonate process;
- Sulfinol process;
- Alkazid process;
- liquid redox processes (e.g. Stretford process); and

These techniques are described in sub-sections (a) - (d) below.

After absorption in an amine or equivalent absorption agent, hydrogen sulphide can be recovered and passed to a sulphur recovery unit for conversion to elemental sulphur. The absorbent stream passes to a regenerator where heat is applied to distil off the hydrogen sulphide and the amine/absorbant is made "lean" for recycle to the scrubber. The top product passes through the column condenser, with condensate returning to the column and the acid gas (which is > 90% H_2S) passing to the sulphur recovery unit.

A typical Claus sulphur recovery unit operating with "split" flow and three catalytic stages operates as follows. Part of the H_2S-containing gas stream is burnt in air in a furnace to produce sulphur dioxide and water vapour. Further hydrogen sulphide then reacts with the sulphur dioxide to produce water vapour and elemental sulphur. Both reactions occur in the combustion stage so the sulphur that is formed there is condensed and removed from the exit gases. Additional H_2S-containing gas is injected in a re-heater and the mixture is passed to the first catalytic stage where the second reaction continues. The reaction,in a fixed bed of bauxite, is equilibrium-limited and overall conversion of hydrogen sulphide and SO_2 to sulphur depends upon the number of reaction and condensing stages. To achieve acceptable conversion, three stages (or two stages and tail gas clean-up) are required - and any residual sulphur dioxide and hydrogen sulphide are passed to tail-gas incineration before discharge to air.

Sulphur recovery plants should be required to operate to a recovery efficiency of at least 98% during normal operation. Three catalytic conversion stages, with the final stage utilising a selective catalyst (eg super Claus process) should achieve this - as should or two catalyst stages and tail-gas treatment in which residual sulphur dioxide is reduced to hydrogen sulphide, and passed through one of the amine (or equivalent) scrubbers. Notwithstanding the effectiveness of these techniques, it may still be necessary to considered further abatement techniques to achieve the required release level. For example, most sulphur recovery units only operate efficiently over a limited throughput range so consideration has to be given to managing throughputs outside this range.

Among developments of Claus recovery systems is Bio-Claus, a process that biologically removes sulphur dioxide from incinerated Claus tail gas. Further detail on Claus sulphur recovery is given in Section 4.23.5 of the Mineral Oil and Gas Refineries BREF (**Ref 1**).

(a) Mono- and di-ethanolamine processes

The amine absorbent passes counter-current to the sour gas in a packed column, and the amine compounds react with hydrogen sulphide and carbon dioxide to form inert compounds. The sweetened gas passes forward for further treatment, and the rich amine stream is transferred to a feed drum, which also separates entrained hydrocarbons.

Methyldiethanolamine (MDEA) features in many of the most modern amine blends as MDEA-based amine systems have a good absorption efficiency and can be tailored to suit particular waste streams.

(b) Hot carbonate process

This process is similar to the ethanolamine processes but the absorbent is potassium carbonate.

(c) Sulfinol process

In order to avoid the degradation losses suffered by MDEA solutions, some plants have switched to the solvent Sulfinol. Sulfinol solution usually consists of 40 - 45 wt% sulfolane (tetrahydrothiophene), 40-55% di-isopropanolamine, with the balance as water. Sulfinol provides greater gas treatment capacity, lower solvent circulation, lower heat requirements, and lower rates of solvent degradation.

(d) Alkazid process

The alkazid process is another cyclic heat regenerative type. It uses "DiK" solution (which contains the K salt of N,N-diethylglycine or N,N-dimethylglycine) which selectively absorbs hydrogen sulphide, carbon dioxide, small amounts of carbon disulphide and hydrogen cyanide. The "M "solution, containing sodium alanine, absorbs hydrogen sulphide and carbon dioxide simultaneously; the "S "solution, containing sodium phenolate, absorbs carbon disulphide and mercaptans more effectively.

Liquid redox processes

Direct sulphur recovery from weak hydrogen sulphide streams by liquid redox provides a viable alternative to amine stripping followed by Claus sulphur recovery.

The relevant liquid redox technologies use a number of mild oxidising agents to oxidise hydrogen sulphide in solution to sulphur and water. The oxidising agents usually contain vanadium (the Stretford process) or iron (the Ferrox process).

The Stretford process is a continuous system that removes hydrogen sulphide from effluent gases and converts it to elemental sulphur. The gas stream is first scrubbed in an alkaline solution containing dissolved vanadates and anthraquinone disulphonic acids, fixing the hydrogen sulphide. The liquid from the scrubbing stage then passes to a reaction tank, where virtually all the hydrogen sulphide is oxidised to elemental sulphur. The next stage separates the sulphur from the solution - which is then returned to the scrubbing stage. The sulphur is floated off as a froth for the final stage of recovery. The sulphur is usually recovered in a pure saleable form from the slurry by melting, filtering and decantation under pressure.

The vanadium-based Stretford process can achieve removal efficiencies of 99.9% and the process is tolerant to fluctuating flowrates. However, the use of vanadium may not always be desirable from an environmental viewpoint, so other redox processes utilising iron-based catalysts have been developed.

2.1.13.4.4 Treatment of sulphide-containing effluents

Where hydrogen sulphide or inorganic sulphides are likely to be in scrubber liquors, wash liquors, etc., the sources should be identified and the liquors treated prior to disposal. Several methods of treatment exist and the most appropriate is largely dependent upon the volumes to be treated as given below.

(a) Steam stripping

Where there are large volumes of aqueous wastes containing hydrogen sulphide, live steam can be injected to strip out the hydrogen sulphide as a vapour. The hydrogen sulphide gas is then treated as described in he previous Section.

(b) Air oxidation

Minor process vents and extraction systems are often scrubbed with sodium hydroxide. The resultant sodium sulphide solution is readily oxidised by passing air through the scrubber - particularly with the addition of catalytic amounts of iron or vanadium salts.

(c) Chemical oxidation

Aqueous streams containing sulphide can be readily treated continuously or batch-wise by a range of oxidising agents. Sodium hypochlorite is commonly used, owing to its price and availability, but hypochlorite addition requires careful control to prevent an excess and the pH should be maintained above 10 to ensure that no free chlorine is generated. The final effluent should be monitored for sulphide, oxidising agent and pH.

(d) Biological treatment

Biological treatment of effluent containing many sulphur compounds is possible, but it is susceptible to shock load. Strict control of conditions is required to prevent formation of hydrogen sulphide.

2.1.14 Phosphorus and its compounds

Phosphorus has not been manufactured in the UK since the early 1970s. It is imported into the country in rail tankers, road tankers, ISO tankers and drums, having been loaded as a liquid, allowed to solidify in transit and then melted for off-loading. Stored phosphorus is blanketed by water or nitrogen, or both.

Different sources of phosphorus will have varying trace levels of arsenic, iron, antimony and organic impurities, which may affect releases to water from phosphorus-using processes. Trace organic impurities can usually be rendered water-soluble so washing the phosphorus removes the organics. These washings along with water used for blanketing phosphorus in storage (known as 'phossy water') can be discharge to the site effluent treatment plant.

2.1.14.1 Phosphorus pentoxide (P_4O_{10}) manufacture

Liquid white phosphorus is atomised and.burnt in a combustion chamber with an excess of air, dried by refrigeration, to produce phosphorus pentoxide vapour. In some cases the air is enriched with oxygen.

$P_4 + 5\ O_2$ ------> P_4O_{10}

The phosphorus pentoxide vapour is cooled and condensed as a solid, collected, and packed into containers.

Traces of moisture in the phosphorus and air lead to the formation of solid deposits of poly-phosphoric acid in the condensing system. These are removed manually and are allowed to hydrolyse slowly to weak phosphoric acid (H_3PO_4) by atmospheric moisture before dispatch to the site effluent treatment plant. Some plants undertake additional drying of combustion air with silica gel to reduce the formation of poly-phosphoric acid

The condenser off-gases comprising excess air, entrained phosphorus pentoxide and small quantities of oxides of nitrogen from the combustion stage, pass to a scrubber where the phosphorus pentoxide is scrubbed out with dilute phosphoric acid, and thence to a mist eliminator and the stack. Droplets of phosphoric acid removed by the mist eliminator are returned to the scrubber, and any surplus phosphoric acid from the scrubber is incorporated in down-stream phosphoric acid production. The efficiency of removal of thermal NO_X in, and its effect on the quality of the product from, the scrubber and demister, need to be carefully evaluated.

Any phosphorus pentoxide that has passed through the scrubber and demister unscathed, will combine with moisture in the atmosphere to form a visible fume of phosphoric acid particles.

2.1.14.1.1 Potential releases from the manufacture of phosphorus pentoxide

Releases to air

- Small amounts of phosphorus pentoxide, from white phosphorus delivery.
- Phosphorus pentoxide and phosphoric acid mist from scrubber and demister stack
- Nitrogen oxides formed during combustion from scrubber and demister stack
- Localised particulate from product handling and package filling.

Releases to water

- Blanket 'phossy' water from liquid white phosphorus storage.
- Phosphoric acid from scrubbing operations.
- Phosphoric acid from the hydrolysis of phosphorus pentoxide cleaned out from solids handling equipment.
- By-product polyphosphoric acid hydrolysed to phosphoric acid.

All releases to water should be via a site treatment plant.

Releases to land

- Calcium phosphate and trace amounts of phosphorus from neutralisation of 'phossy' water and dilute phosphoric acid with lime.

2.1.14.2 Phosphine (PH_3) manufacture

Phosphine (PH_3) can be manufactured from phosphorus by a number of routes, including:

- Acid-catalysed reaction of red phosphorus with steam;
- Electrolytic reduction of white phosphorus;
- Co-production with hypophosphites from alkali and phosphorus;

2.1.14.2.1 Acid-catalysed production of phosphine

Liquid phosphorus is fed continuously into a reactor containing phosphoric acid, and maintained under an inert atmosphere by a nitrogen purge. Steam is injected into the reactor and phosphine gas is continuously evolved. The process is operated at slightly positive pressure to prevent air ingress and the potential for explosion.

$2 P_4 + 12 H_2O$ -------> $5 PH_3 + 3 H_3PO_4$

The gaseous phosphine product contains about 1-2% of hydrogen formed by a competing reaction of phosphorus with steam (shown below), together with 3-5% nitrogen from blanketing of the reactor.

$P_4 + 16\ H_2O$ --------> $10\ H_2 + 4\ H_3PO_4$

Unreacted phosphorus vapour in the phosphine leaving the reactor is condensed and recycled as liquid feed, and the phosphoric acid co-product is withdrawn periodically. The phosphine gas product is stored in a water-sealed gas holder.

To prevent pressure relief resulting in significant phosphine releases to atmosphere, reliable instrumentation should shut down the process in the event of minor pressure excursions, and vent lines should be routed to a tail-gas incinerator and/or alkali/ hypochlorite scrubber or an emergency flare

2.1.14.2.2 Electrolytic production of phosphine

A diaphragm electrolytic cell can produce phosphine by the direct reduction of elemental phosphorus dispersed in an electrolyte - which, in both the cathodic and anodic sections, is phosphoric acid solution, operating at temperature between 60 °C and 100 °C Phosphine is evolved at the cathode and metals such as mercury, cadmium amalgam or lead are suitable for the cathode. The cathode reaction is:

$P_4 + 12\ H^+ + 12\ e^-$ -------> $4\ PH_3$

Use of a diaphragm and careful design and operation at the surface of the cathode minimises hydrogen production. Oxygen is released at the anode - which is likely to be graphite or stainless steel, as the use of heavy metals like mercury, cadmium or lead inevitably figure in the releases.

2.1.14.2.3 Co-production of phosphine and sodium hypophosphite

Phosphine is also generated as a by-product in the production of sodium or calcium hypophosphite by alkali-catalysed disproportionation:

$P_4 + 3\ NaOH + 3\ H_2O$ ---------------> $PH_3 + 3\ NaH_2PO_2$

Calcium hydroxide is the alkali in the production of calcium hypophophite., of course.

2.1.14.2.4 Potential releases from phosphine production

Releases to air

- Small amounts of phosphorus pentoxide, from white phosphorus delivery.
- Phosphine from air blowing of liquid streams.
- Phosphine from pressure relief and other vents.

Releases to water

- 'Phossy' water from liquid white phosphorus storage.
- Phossy' water from condensing white phosphorus vapour.
- Water from phosphine gas holder seal.
- Alkaline or hypochlorite scrubbing liquors.
- Filter aid from by-product phosphoric acid filtration.

Releases to land

- Calcium phosphates and small amounts of phosphorus from treatment of liquid effluent streams.

- Arsenic and antimony may be present in scrubbing liquors (as well as in co-product phosphoric acid) if present in the phosphorus feedstock. The destination of all cationic impurities in the phosphorus must be evaluated.
- Used filter cartridges.

2.1.14.3 Phosphorus trichloride (PCl_3) manufacture

Phosphorus trichloride is produced by the direct union of phosphorus and chlorine:

P_4 + 6 Cl_2 --------> 4 PCl_3

Liquid white phosphorus and gaseous chlorine are fed to a stirred reactor containing phosphorus trichloride liquid, with phosphorus being kept in excess in the reactor. Phosphorus trichloride vaporised by the heat of reaction leaves the reactor and passes up through a distillation column and reflux condenser. The majority of the condensate is returned to the column as reflux, with the remainder passing to product storage from the overhead receiver.

Gaseous emissions from the process consist principally of phosphorus trichloride vapour, the quantity passing to the scrubber being dependent on the performance of the condensers. Some hydrogen chloride, produced from trace water in the phosphorus feedstock, is also present in the off-gases which are generally scrubbed with water to give hydrochloric acid and phosphorous acid (H_3PO_3) by hydrolysis. Same installations use sodium hydroxide scrubbers and others, where there is sharing of the scrubbing facilities with phosphorus oxychloride ($POCl_3$) manufacture, a water scrubber is followed by a sodium hydroxide scrubber.

Phosphorus trichloride storage vessels are vented to a scrubber system, usually that of the reaction system, and drum filling operations are provided with local air extraction around the filling nozzle, and this extraction is also scrubbed.

Overhead condenser practices vary with regard to coolant. Cooling water can be used but with pressurised water there is a risk of water ingress and violent reaction - so gravity-driven falling film designs can be used to minimise this risk. Alternatively, inert heat transfer fluid or air-cooled condensers may be used.

Pressure relief of the reaction system should be by bursting disc/protected relief valve assembly to the scrubbing system or by bursting disc to an expansion or containment vessel which, in turn can vent directly or via another relief device to the scrubbing system.

Impurities present in the phosphorus feedstock accumulate in the reactor and have to be periodically removed and the reactor cleaned. These residues include arsenic trichloride, antimony trichloride, and 'coked' organics from initial trace impurities in the phosphorus. By-product phosphorus oxychloride (owing to oxygen impurity in the chlorine) may also be present. After distilling out the remaining phosphorus trichloride, cold water or dilute sodium hydroxide is added carefully to the reactor to decompose all residual acid chlorides - and the resulting liquor is discharged under controlled conditions to the effluent treatment plant.

2.1.14.3.1 Potential releases from phosphorus trichloride manufacture

Releases to air

- Small amounts of phosphorus pentoxide, from white phosphorus delivery.
- Phosphorus trichloride vapour from reactor, tank filling and breathing, drum filling, vent pressure relief and stirrer glands.

- Hydrogen chloride from reactor and scrubbers.
- Chlorine from pressure relief.
- Phosphorus oxychloride and arsenic trichloride from distillation of reactor residues.

Releases to water

All aqueous discharges should pass to a site treatment plant.

- Blanket 'phossy' water from liquid white phosphorus storage.
- Phosphorous acid and hydrochloric acid from wet scrubbing of phosphorus trichloride vapours.
- Metal, arsenic and antimony oxides or salts, and 'coked' organics from cleaning reactors.

Releases to land

- Calcium phosphate and small amounts of phosphorus from site effluent treatment plant.

2.1.14.4 Phosphorus oxychloride ($POCl_3$) manufacture

Phosphorus oxychloride can be manufactured by two routes - the "chlorination process" and the "oxygen process".

2.1.14.4.1 Chlorination process for phosphorus oxychloride manufacture

$POCl_3$ is produced in batch by chlorinating a mixture of phosphorus pentoxide and phosphorus trichloride with gaseous chlorine. Thus:

$6 PCl_3 + P_4O_{10} + 6 Cl_2$ -------> $10 POCl_3$

A measured quantity of phosphorus pentoxide is dispersed in phosphorus trichloride in a stirred reactor and chlorine is then bubbled through the mixture. Exothermic heat is removed by evaporating and refluxing phosphorus trichloride via a distillation column and overhead condenser, with non-condensed vapours pass to a scrubbing system. As the batch reaction proceeds the phosphorus trichloride in the reflux is progressively replaced by phosphorus oxychloride.

When the reaction is complete the chlorine supply is stopped and the batch is refluxed to drive off traces of free chlorine to the scrubber system. The phosphorus oxychloride is then distilled from the reactor to the overhead receiver and thence to storage.

After a number of batches, residues accumulating in the reactor are removed by water washing. Hydrogen chloride generated by hydrolysis of chlorinated phosphorus compounds is directed to the scrubber system, and the washings comprising residual dilute hydrochloric acid, metal chlorides and phosphoric acid, are directed to the site effluent plant.

2.1.14.4.2 Oxygen process for phosphorus oxychloride manufacture

Phosphorus trichloride is oxidised to $POCl_3$ by oxygen or air - batch-wise or in a continuous process.

$2 PCl_3 + O_2$ -------> $2 POC1_3$

In batch operation, phosphorus trichloride is added to the stirred reactor and air or oxygen bubbled through the liquor. The heat of reaction is removed by evaporation of the PCl_3, and then the $POCl_3$, to reflux condensers. Off-gases from the reflux condenser pass through an after-condenser cooled by refrigerant to maximise the retention of phosphorus halides, before being directed to wet scrubbing. Once the reaction is complete, the air or oxygen supply is stopped and the phosphorus oxychloride product is filtered and sent to storage.

The equivalent process can be carried out continuously, and this technique avoids large temperature increases. Phosphorus trichloride and oxygen are passed co-currently through a water-cooled packed column. Product leaves this column with unreacted phosphorus trichloride at about 35 ºC and is passed to the top of a second column for further reaction with oxygen. Excess oxygen leaves via a cold trap for removal of phosphorus oxychloride and passes on to a wet scrubber system.

Wet scrubbing of vent gases involves either water or sodium hydroxide scrubbers or both. At sites where both phosphorus oxychloride (either route) and phosphorus trichloride are manufactured, a single scrubber installation tends to be used for both plants.

2.1.14.4.3 Potential releases from phosphorus oxychloride manufacture

Releases to air

- Phosphorus trichloride vapours from reactor charging, tank filling, breathing and pressure relief systems via wet scrubbers.
- Phosphorus oxychloride vapours from reactor, distillation, product storage and pressure relief systems via wet scrubbers.
- Chlorine from chlorine handling systems, reaction slip and pressure relief systems via wet scrubbers.
- Hydrogen chloride from wet scrubbers.

Releases to water

All aqueous discharges should pass to a site treatment plant.

- Liquors from wet scrubbing of chlorine gas (sodium hypochlorite) and vapours of phosphorus halides (hydrochloric, phosphoric acid and phosphorous acid).
- Phosphorus pentoxide spillages, hydrolysed with water to phosphoric acid.
- Acidic water from washing reactors, may contain traces of arsenic, antimony and nickel chlorides.

Releases to land

- Calcium phosphate from treatment of liquid effluent streams.

2.1.14.5 Phosphorus pentasulphide (P_4S_{10}) manufacture

Phosphorus pentasulphide is produced by the direct union of white phosphorus and sulphur:

White phosphorus and sulphur are added as liquids in stoichiometric amounts from measure vessels to a pre-charge of liquid phosphorus pentasulphide in a reaction vessel. The elements react readily to form phosphorus pentasulphide and, after initial heat is supplied at start-up, the reactor is maintained at 380 ºC - 400 ºC by cooling. An inert gas atmosphere (carbon dioxide or nitrogen) is maintained in the reaction vessel and phosphorus pentasulphide vapours are condensed in the vent system for reflux back to the reactor. Before release to atmosphere, the vent gases are burnt to convert traces of hydrogen sulphide to sulphur dioxide.

Phosphorus pentasulphide liquid is fed to a flaker and the flake product is transferred by a cooled screw conveyer for storage or packing Some of the flaked product is milled to a powder and also packed, with any recovered dust returned for reprocessing. The packing operation has local air extraction and the flaker, grinder and conveyor are operated under an inert gas blanket, which vents through a water seal. Water from the seal is discharged to site effluent.

If organic impurities are present in the reactants, the product may need to be purified by (vacuum) distillation. The distillation residue often contains arsenic sulphides and metal sulphides and these are usually disposed of to landfill.

2.1.14.5.1 Potential releases from phosphorus pentasulphide manufacture

Releases to air

- Hydrogen sulphide from reactor vent and sulphur storage.
- Phosphorus pentasulphide particulates from flaking, grinding and product packaging.
- Oxides of sulphur from combustion of hydrogen sulphide.

Releases to water

- 'Phossy' water from liquid white phosphorus storage.
- Hydrogen sulphide in the water from water seals.

Releases to land

- Phosphorus pentasulphide from spillages and cleaning of solids handling equipment.
- Residues from the distillation unit.
- Calcium phosphate and small amounts of phosphorus from site treatment plants.

2.1.14.6 Phosphorous acid (H_3PO_3) manufacture

Phosphorous acid is produced by the controlled hydrolysis of phosphorus trichloride:

$PCl_3 + 3\ H_2O$ -------> $H_3PO_3 + 3\ HCl$

The reaction can be violent and two separate process technologies have been developed to overcome this problem - liquid-phase hydrolysis and vapour-phase hydrolysis.

2.1.14.6.1 Liquid-phase hydrolysis of PCl_3

Phosphorus trichloride and dilute HCl are added continuously to an agitated reaction vessel. Hydrogen chloride evolved by the reaction is absorbed in water and recovered as a by-product acid. The phosphorous acid/hydrochloric acid mixture overflows from the reaction vessel to an evaporator where the hydrogen chloride is distilled-off and recovered in a strong acid absorber. The concentrated phosphorous acid is solidified on a flaker and then transferred by screw-conveyor for packaging. The flaking and packaging operations are enclosed and performed with local extraction.

The hydrogen chloride from the reactor or evaporator is cooled and demisted to remove entrained droplets before being absorbed in a conventional cooled strong acid absorber in series with a weak acid tail-gas scrubber. Bursting disc pressure relief from the reaction vessel passes via a drench scrubber to atmosphere.

2.1.14.6.2 Vapour-phase hydrolysis of PCl_3

Phosphorus trichloride liquid and water are atomised with steam in a coaxial atomiser and fed downwards into a reaction vessel at 150 ºC, with additional steam being supplied to the reactor vessel to assist mixing. The vapours pass to a direct contact condenser-separator fed with phosphorous acid and the condensate then passes to a vertical evaporator where most of the hydrogen chloride distils-off. Concentrated phosphorous acid from the bottom of the evaporator is stripped of residual hydrogen chloride in a counter-current by nitrogen, and the pure concentrated phosphorous acid is sent to the flaker.

As in the liquid-phase process concentrated hydrochloric acid is a by-product, with hydrogen chloride in the tail-gas absorber vent essentially being the only gaseous release. In the vapour-phase process, the tail-gas absorber design must cater for the nitrogen stripping gas flow which will leave the absorption system saturated with HCl and which will potentially increase the hydrogen chloride loss - but the management and recovery of acid streams is generally less complicated than for the liquid-phase hydrolysis process.

Phosphine is a possible thermal decomposition product of phosphorous acid if the process is operated close to its thermal decomposition temperature.

2.1.14.6.3 Potential releases from phosphorous acid manufacture

Releases to air

- Hydrogen chloride from reaction, evaporation and stripping systems.
- Phosphorus trichloride vapour from feedstock storage.
- Phosphine from reaction by thermal decomposition in abnormal operation.
- Particulates from flaking and product drum filling.
- Phosphorus trichloride and hydrogen chloride vapour from pressure relief drench scrubber system.

Releases to water

All releases should pass to an effluent treatment plant.

- Liquors from wet scrubbing of vents from phosphorus trichloride storage.
- Surplus weak hydrochloric acid.
- Wash-downs and spillages, cleaning of solids handling equipment.

Releases to land

- None.

2.1.14.7 Phosphorus pentachloride (PCl_5) and Aryl phosphonic acid manufacture

2.1.14.7.1 Production of phosphorus pentachloride (PCl_5)

Phosphorus pentachloride (PCl5) is produced batchwise in an organic solvent either for captive use as an intermediate in the production of aryl phosphonic acids ($RPO(OH)_2$) (see below) or for sale in solid form.

PCl_5 is produced by the direct reaction of excess chlorine with phosphorus trichloride. Phosphorus trichloride is dissolved in about an equal volume of solvent in the reactor equipped with an agitator, cooling jacket and reflux condenser. Chlorine gas is admitted and,as the reaction proceeds, crystals of phosphorus pentachloride form and are suspended in the solvent. The operation takes place under total reflux, reaction heat being removed both by evaporation and by the reactor cooling jacket.

Vapour emissions from the reflux condenser are passed to a chilled or refrigerated condenser to recover solvent and then to water and sodium hydroxide scrubbers to remove phosphorus trichloride and chlorine respectively.

If required, the suspended phosphorus pentachloride can be isolated by filtration with the solvent recovered as filtrate, clarified and returned for re-use. The PCl_5 crystals are dried of solvent by circulating hot water through the jacket of the filter, and the product packaged for sale.

In an alternative continuous process not involving a solvent, phosphorus trichloride is fed to the top of a counter-current reaction column, with chlorine fed in the bottom. Phosphorus pentachloride is formed and collects at the bottom of the column where it is separates and is extracted by mechanical screw.

2.1.14.7.2 Manufacture of aryl phosphonic acids ($R'PO(OH)_2$)

The product slurry of PCl_5 and solvent is directly reacted with an aromatic, and then the chlorinated phosphorus intermediate is hydrolysed to generate the substituted phosphonic acid:

$R'H + PCl_5$ -------> $R'PCl_4 + HCl$

$R'PCl_4 + 3\ H_2O$ ------> $R'PO(OH)_2 + 4\ HCl$

The aromatic is added to the PCl_5 slurry at a controlled rate with the temperature controlled by cooling. The hydrogen chloride and then the solvent are removed by raising the temperatures and evaporation to condensers and scrubbers. Condensed solvent is recovered and stored for re-use; the hydrogen chloride is absorbed in water and stored for re-use or sale, or neutralised and discharged as effluent.

The intermediate compound together with any residual phosphorus pentachloride is hydrolysed with water at a controlled rate, generating a slurry of phosphoric acid and the product aryl phosphonic acid. The product is filtered off and packaged for sale as semi-dry filter cake. The filtrate containing the phosphoric acid is dispatched to effluent treatment.

2.1.14.7.3 Potential releases from aryl phosphonic acids manufacture

Releases to air

- Chlorine from reaction and pressure relief to sodium hydroxide scrubber.
- Phosphorus trichloride and chlorine from storage, reaction and pressure relief.
- Hydrogen chloride from reaction and scrubbers.
- Chlorinated solvent from storage, reaction, pressure relief, condensers and scrubbers.
- Aromatic organic from storage and pressure relief.

Releases to water

- Liquors from wet scrubbing of phosphorus trichloride vapour and chlorine gases containing hydrochloric acid, phosphorous acid, sodium hypochlorite and chlorinated solvents.
- Hydrochloric and phosphoric acids and chlorinated solvent from filtration.
- Aryl phosphonic acid from cleaning of filter and solids handling equipment.

Releases to land

- None.

2.1.14.8 Alkyl/aryl phosphates manufacture

2.1.14.8.1 Aryl phosphate esters ($(R'O)_3PO$)

For aryl phosphate esters, depending on the product desired, the aryl component may be a single compound (e.g. a particular alkylated phenol) or a mixture (e.g. cresol and xylenol) - and these are reacted with phosphorus oxychloride in a batch reactor. The phenol(s) and a catalyst are charged to the reactor and heated to the required temperature before phosphorus oxychloride is metered in.

$3R'OH + POCl_3$ --------------> $(R'O)_3PO + 3\ HCl$

The reaction generates hydrogen chloride, which is directed to an absorber and tail-gas scrubber, and the recovered 32-34% HCl is re-used or sold. Residual HCl in the ester product is stripped out at elevated temperature and absorbed in water - which usually has to be discharged to an effluent treatment plant.

The crude product is transferred to intermediate storage tank prior to distillation. In the distillation units, excess phenolics are distilled off first and are recovered for re-use. The product is then distilled off and passes to a steam stripping column to improve the colour of the product and remove any residual trace of phenolics. The steam is condensed and residual organics separated and recovered, the water becoming part of the aqueous discharge from the plant. The final product is transferred to storage and the residues from the first distillation containing waste organics, including the catalyst, are drawn off and drummed for dispatch as waste.

Storage and tanker discharge of the raw material phosphorus oxychloride involves padding with nitrogen - and this flow is vented through a water scrubber.

2.1.14.8.2 Mixed phosphate esters ($(R'O)_2(RO)PO$)

For mixed aryl/alkyl phosphate esters, in an analogous reaction to the one above, phosphorus oxychloride is reacted first with an alcohol to substitute one chlorine atom, and then with a phenol to substitute the other two chlorine atoms:

A measured amount of phosphorus oxychloride is charged to a stirred reactor and then the alcohol is added at a controlled rate, the process operating with a cooled recycle to control the temperature. When the reaction stage is complete the hydrogen chloride is stripped off to a scrubber where hydrochloric acid is produced for re-use or forms part of the aqueous discharge from the plant.

In a separate reactor, phenol is reacted with 47% sodium hydroxide solution and water to produce sodium phenate. and then the mono-alkylated phosphate ester is introduced to the sodium phenate at a controlled rate, the temperature of the reaction being controlled by cooling:

$ROPOCl_2 + 2\ R'ONa$ --------> $(R'O)_2(RO)PO + 2\ NaCl$

The crude ester product is washed to remove the salt, the washings passing to effluent treatment, and then steam-stripped to remove trace organics, the steam being condensed and passed to effluent treatment. The ester product is then filtered and sent to storage.

2.1.14.8.3 Potential releases from the manufacture of alkyl/aryl phosphates

Releases to air

- Hydrogen chloride from reactor, scrubber and pressure relief.
- Phosphorus oxychloride from reactor, storage and pressure relief.
- Phenols from storage, reactor, distillation, stripping and pressure relief.
- Alcohols from storage, reactor, scrubber and pressure relief.
- Dichlorinated mono-alkylated phosphate ester from reactor.

Releases to water

- Hydrochloric acid from scrubbers.
- Phenols from scrubbers, strippers and washing
- Alcohols from stripping and washing.
- Alkyl/ aryl phosphate esters from washing.
- Trace amounts of chlorinated organics.

Releases to land

- Distillation residues, principally inert catalyst with aryl phosphate esters, and high-molecular weight organics, which may be chlorinated.
- Charred organics from filter.

2.1.14.9 Control measures for phosphorus compounds

2.1.14.9.1 Use and handling of phosphorus compounds

(a) Phosphorus pentoxide (P4O10)

Phosphorus pentoxide is neither combustible, nor supports combustion, but it does react very vigorously with moisture, producing heat, acid and steam. Without moisture present, no fire or combustion hazard exists.

Drums storing phosphorus pentoxide must be air- and moisture-tight at all times. When empty drums are disposed of, all traces of P_4O_{10} should be removed, since any remaining material will hydrolyse to phosphoric acid and severe corrosion may result.

Piping and vessels used for the transfer of phosphorus pentoxide storage should be constructed of 316L stainless steel with PTFE gaskets or equivalent and designed to eliminate any contact with atmospheric moisture e.g. by equipping vents with dryers or by continuously purging the system with dry air or inert gas.

(b) Phosphorus trichloride (PCl3) and phosphorus oxychloride (POCl3)

PCl_3 can be safely stored in carbon steel tanks with a small purge of dry nitrogen to exclude moisture and prevent hydrolysis of PCl_3 to form phosphorous acid and HCl. Storage of $POCl_3$, however, requires more sophisticated materials of construction than PCl_3. Carbon steel and stainless steel are not suitable for long-term $POCl_3$ and for its storage only glass-lined steel or nickel tanks are recommended. Piping may be nickel, glass, glass-lined steel or PTFE-lined steel, with PTFE-lined plug or ball valves normally in use.

The off-loading of PCl_3 or $POCl_3$ causes fume to be expelled from the stock-tank so the use of a water- or alkali-scrubber is considered mandatory. The piping must be designed such that the scrubber cannot flood and back up into the storage vessel. Similarly, overfilling the storage tank so that liquid PCl_3 or $POCl_3$ enters the scrubber will create a violent reaction producing HCl, phosphoric acid, phosphine, physical damage and possibly fire. High level trips, elevated vent ducts and overflow catch-tanks should all be considered.

(c) Phosphine

Given the toxic and explosive properties of phosphine, storage should be designed to contain as small an inventory as practicable. It is also important to prevent oxygen ingress into phosphine production or handling plant since this would present an explosion hazard. Processes should therefore be operated at slight positive pressure, with water seals between plant items and capture devices or the environment.

2.1.14.9.2 Control of releases to air

The main releases to air from phosphorus processes are phosphorus compounds (especially phosphine, phosphorus pentoxide), HCl fume, chlorine, hydrogen sulphide and light organics. The actual pollutants and their concentrations will depend on the process involved Typical control techniques for these compounds are given below:

- Absorption into water for removal of hydrogen chloride - the resulting hydrochloric acid may be sold, used in other processes or used for pH correction in the site effluent treatment plant.
- Caustic scrubbing for treatment of HCl fume not removed by absorption into water.
- Thermal oxidation - careful design is required to ensure the destruction of mercaptan odour. A support fuel is normally burnt to maintain the desired temperature. Thermal oxidation is often followed by an absorption unit to remove certain combustion products, e.g. phosphorus pentoxide from combustion of phosphine.

Fugitive emissions may be minimised by employing pressurised seals on agitated vessels, and the use of glandless pumps for transfers of fuming liquids, where possible.

2.1.14.9.3 Control of releases to water

Aqueous phosphate emissions should be prevented from reaching controlled waters by precipitation with lime to produce insoluble calcium phosphate, and the resulting sludge sent for landfill.

Effluents from phosphine plants should be blown with air to remove dissolved phosphine and then neutralised before passing to an effluent treatment system - with the air from the effluent stripping being routed to a phosphine abatement/destruction facility.

2.1.15 Use of As, Be, Ga, In, Pb, Pd, Pt, Sb, Se, Te, Tl and their compounds

There is a wide range of activities involving antimony, arsenic, beryllium, gallium, indium, lead, palladium, platinum, selenium, tellurium, thallium to their compound which potentially fall to PPC regulation in this sector of the Inorganic chemicals industry. Applications range from laboratory scale through to major chemical production and from high-technology applications to mature industries over a hundred years old. End-use applications covered by this sector include lead acid batteries, semiconductor devices, colours/pigments, lighting, PVC stabilisers, PVC compounds, wood preservatives, precious metal coatings, etc.

Outlined below are some examples of processes encountered in this sector of the industry.

2.1.15.1 Manufacture of certain oxides

Oxides of several of the elements covered by this section are important industrially. For example, antimony and lead oxides are produced in large quantities by the oxidation or roasting of the element or prepared concentrates. Manufacture may be carried out by continuous or batch methods in a variety of types of furnace or kiln, and the scale of the process varies to suit the demand for the product. Furnaces are typically gas-fired although some are oil-fired.

2.1.15.1.1 Manufacture of Antimony oxide

Antimony oxide is manufactured by the roasting of antimony oxide concentrates with antimony metal. The reaction involved is:

$4\ Sb + 3\ O_2$ -------> $2\ Sb_2O_3$

The process is carried out in direct-fired continuous rotary kilns operated so as to volatilise the product, which is then condensed and collected using fabric filters. After separation the antimony oxide is purified by revolatilisation in further rotary kilns followed by collection of the pure product, blending and packing. The slag formed during furnacing contains lead and where practicable is sent for smelting.

Special hygienic grades of product are made by damping, pasting or granulating antimony oxide with suitable plasticisers, water or waxes.

2.1.15.1.2 Manufacture of Lead oxides

The lead oxides, litharge (lead (II) oxide, PbO) and red lead (dilead (II) lead (IV) oxide, Pb_3O_4), are manufactured by a two-stage oxidation process. The first stage is common to both oxides and involves feeding lead into a stirred reaction pot in which the exothermic reaction maintains the required temperature as controlled by the feed rate of fresh lead. An impure form of lead oxide is produced, containing a mixture of the element and the monoxide, dioxide and red lead:

$2\ Pb + O_2$ ------------> $2\ PbO$

$Pb + O_2$ -------------> PbO_2

The mixed product is carried by the air stream to a collecting system of cyclone, fabric filter and HEPA filter. It is then processed in the second stage by heating in a gas- fired furnace in which the conditions can be varied to produce the pure form of product required, either litharge or red lead:

$6\ PbO + O_2$ ------------> $2\ Pb_3O_4$

$2\ PbO_2 + Pb$ -----------> Pb_3O_4

Lead acid battery grade oxide

The major use of lead worldwide (over 60%) is for the lead acid batteries. The Shimadzu process is the principal process used for the production of lead oxide, and this employs continuous partial oxidation of lead pellets to give a closely controlled and intimate mixture of the element and lead monoxide/ suboxide (PbO/ Pb_2O). Small cylindrical lead pellets are cast and then tumbled in a rotary mill drum, generating frictional heating, where they gradually react with air. The product is in the form of fine microcrystalline lead oxide particles, each with a core of unconverted lead. These particles are carried out of the drum in the air stream to a collecting system typically consisting of a cyclone, fabric filter and HEPA filter.

Shimadzu plants are supplied by specialist contractors and typically consist of a number of mills and collecting systems, which are capable of automatic control and semi-remote operation from a common control panel. The plants should incorporate alarmed pressure and temperature monitors. Fire detection should be installed as fires can result from overheating of the product.

There are variations of the Shimadzu battery-grade lead oxide process outlined above. For example, the air-swept mill drum may be replaced by a perforated screen-mill drum in which product particles of the desired size fall through the perforations of the drum and are then classified by sieves before collection. In another variation, the oxidation is carried out in a reaction pot similar to those used in the first stage of litharge and red lead manufacture.

Battery manufacturers have their own specifications for the product oxide, though a typical PbO content would be 70%. Because of the importance of oxide quality control to the finished batteries, the majority of manufacturers have an in-house plant, although some smaller facilities use bought-in material. Some traction batteries and stand-by power batteries use red lead, which is made as described above.

In the battery industry, other associated activities involving lead or lead comounds - such as, lead melting and casting for plates and terminals, paste mixing, electrode plate pasting, flash drying, curing, stacking and insertion into battery cell containers - may or may not be within the PPC installation; it will depend on their potential for releasing lead into the air (and being listed activities in their own right) and, if not listed activities, whether they are directly-associated activities which serve activities which are listed.

2.1.15.1.3 Potential releases from the manufacture of the above oxides

Emissions to air

- Where there is direct-firing, products of combustion, i.e. oxides of sulphur, carbon and nitrogen.
- Particulate matter from furnacing and other operations involving metals and their compounds.
- Ventilation of lead processes to meet workplace air standards, including melting/casting and battery electrode plate production and assembly, may release lead in environmentally significant amounts.

Emissions to water

- Cooling water discharges.
- Dissolved and suspended solids containing heavy metals, from wash waters.
- Dissolved metal compounds in filtrates from activities carried out in aqueous solution.
- Spent scrubber liquors containing e.g. lead compounds, where wet scrubbers are used to abate releases to air.

Emissions to land

- Some furnace wastes may require disposal where the useful content is low.
- Wherever practicable, solid wastes recovered from fabric filters are recycled and slags should be reprocessed to recover useful heavy metals e.g. by smelting.

2.1.15.2 Manufacture of other compounds

Both physical and chemical processes are used in the manufacture of compounds of the elements covered by this section. The majority are batch operations, and the scale of the processes varies from sizeable dedicated facilities to minor products made by campaign working of multi-purpose plant.

2.1.15.2.1 Other lead products

A number of lead compounds are manufactured for applications such as stabilisers in the production of PVC, mirror backing paints, brake linings and pigments.

One group of compounds includes **lead sulphate, phosphite, stearate, phthalate and carbonate** (white lead), each produced in a number of basic forms ranging from monobasic to tetrabasic. They are produced by reacting litharge (made as outlined in **Section 2.1.15.1.2** above with the appropriate acid. For example, monobasic lead sulphate production (lanarkite) follows the stages below:

- A slurry of litharge in water is prepared in a stirred batch reactor and the required quantity of sulphuric acid is added:

$PbO + H_2SO_4$ ---------------> $PbSO_4.PbO + H_2O$

- The resulting basic sulphate slurry is transferred and dewatered by centrifuging or vacuum filtration to give a pulp. This may be mixed with a proportion of previously dried product to reduce the water content.
- The pulp is flash dried in a hot air column drier.
- The compound can then be transferred to mixers in which additives are mixed to form a blended composite mixture for PVC processing.

Another lead compound, **lead chromate**, is produced in red and yellow pigment shades by a simple two-stage process that begins with the reaction of lead with nitric acid to give lead nitrate. This is then reacted with sodium chromate to produce lead chromate. The desired colour shade is obtained by using appropriate additives and the product lead chromate is coated to enhance the physical properties. It is then filtered, dried, ground and classified before packing.

2.1.15.2.2 Antimony sulphide

Antimony sulphide is made by dissolving the antimony-bearing raw materials at predetermined pH and temperature prior to precipitating the desired variety of antimony sulphide.

The antimonial slurry is washed to remove any soluble salts and then filtered, with the resulting cake being transferred to the drying system. After drying to a moisture content of less than 1%, the product may be milled, and then packaged.

Any gases that are evolved during reactions or precipitations are exhausted to caustic scrubbers.

2.1.15.2.3 Platinum and palladium compounds

Palladium and platinum compounds are made by similar processes to the examples above. For example, **palladium chloride** is manufactured in batch by reacting the element with chlorine in hydrochloric acid. The solution of palladium chloride is evaporated to give a crystalline product which is then milled to a powder.

Chloroplatinic acid, an important intermediary in the platinum industry, is made by the chlorination of recovered or refined platinum-group metals in solution, again using a hydrochloric acid medium. The product solution is filtered and evaporated to an appropriate strength for further processing, such as precious metals extraction or catalyst manufacture

2.1.15.2.4 Potential releases from the above wet batch processes

Emissions to air

- Excess gaseous reactants or evaporated media, e.g. chlorine and hydrochloric acid in the manufacture of palladium and platinum compounds.
- Particulate matter containing metal compounds, e.g. lead compounds in the exhaust air from flash drying and packing points.

Emissions to water

- Many of these processes generate process effluent liquors containing metals and their compounds in solution and suspension.
- Mineral acids and other substances used in specific processes.
- Spent scrubber liquors containing e.g. lead compounds, where wet scrubbers are used to abate releases to air.

Emissions to land

- Precipitated sludges and residues from aqueous effluent treatment processes containing metal compounds. These should be reprocessed to recover useful heavy metals wherever practicable.
- Dust recovered from hygiene dust units, where this cannot be recycled or reprocessed.
- Impurities removed from products by filtration.

2.1.15.3 Compound semiconductor manufacture

Several of the elements covered by this section are used in the manufacture of microelectronic semiconductor devices for advanced technology applications, especially in optical and opto-electronics communications, lasers and special integrated circuits. Principally involved are arsenic and gallium, but indium, phosphorus, antimony, selenium and tellurium are also used. One of the main semiconductor areas represented is the use of binary III-V materials (i.e. groups of the periodic table for the two elements used) as substrate wafers on to which successive thin-layer micro-circuits are deposited, and these substrates can provide improvements over silicon wafers in specific applications.

Manufacturing processes based on silicon wafer technologies are less likely to lead to the release of substances covered by this section but, like some III-V substrate manufacture, they may involve the use and release of hydrogen halides and so be listed activities under that description.

The micro-circuits are created by the deposition of thin (about l micron) epitaxial layers on the substrates using materials that include some of the elements listed above. This is followed by various material removal stages together with circuit linking and other operations to produce the required devices. Repeated cleaning and rinsing stages are necessary and use, for example, acids and halogenated hydrocarbon solvents.

Although the scale of the processes used in the microelectronics industry is very small, this is compensated for by the complexity of the plant installations and the toxic and polluting nature of many of the materials used. In particular, the gaseous hydrides arsine and phosphine are used on most sites for circuit deposition and reliable abatement techniques and operating procedures are essential. An Environmental Code of Practice has been published on behalf of the UK microelectronics industry and operators should be expected to adopt this as a part of their approach to environmental management.

2.1.15.3.1 Substrate wafer production

Single crystals of III-V wafers are produced from a number of combinations of elements, principally gallium-arsenic but also indium-phosphorus, indium-arsenic, gallium-antimony and indium-antimony. The processes used involve the growth of a crystal of the desired material by reaction between the constituents, which are brought together with one in liquid phase and the other in the solid or gas phase.

For example, gallium arsenide wafers have been made by the liquid encapsulated Czochralski (LEC) process and the gradient freeze technique:

Liquid encapsulated Czochralski (LEC) process - The gallium arsenide is synthesised in molten form from liquid gallium and solid arsenic in a crucible heated by radio-frequency induction and contained in a sealed pressure vessel. A layer of inert liquid boron trioxide is used to encapsulate the melt, and the vessel is filled with argon with the compound held just above the melting point. Crystal growth is achieved by rotating a seed crystal so that it just touches the melt, and slowly withdrawn it as fresh material deposits.

The raw crystal is heat treated and then undergoes finishing operations, including grinding and slicing, chemical etching, polishing and packaging. Typical end-products are circular wafers of diameter 50-150 mm and up to about 600 microns in thickness.

Gradient freeze technique - An alternative method for the growth of single crystals is the gradient freeze technique in which the two elements are heated together in a two-zone resistance furnace to synthesise the compound. The crystal is formed by a controlled cooling, which is started from one end of the melt and does not use a seed crystal. Subsequent finishing operations are similar to those used by the LEC method.

2.1.15.3.2 Production of deposited circuits

Thin-layer micro-circuits are formed on wafer substrates by the deposition of successive layers of compound semiconductor materials. The principal process employed involves the passing of sequenced reactant and dopant gases over the wafer at high temperature and low pressure in a graphite susceptor reactor heated by radio-frequency induction or high-intensity visible light -which results in the surface deposition or doping of micron or sub-micron layers of the materials in a defined epitaxial alignment. Deposition can be restricted to specific sites by photolithographic preparation of the wafer or by subsequent removal from unwanted sites.

The operation is housed inside glove-boxes and is typically automatically controlled for deposition of an appropriate sequence of materials to provide the desired layering. The materials, which are of high purity, are usually obtained from gas cylinders in remote storage cabinets and piped to the reactor via flow restrictors and control valves. Hydride gases may be supplied in dilute form (e.g. 15% arsine in hydrogen carrier gas) or as 100% gas. Gallium and indium are in liquid organic compound form, i.e. as trimethyl or triethyl compounds, and delivered as vapour by a carrier gas passed through the liquid. Other dopants may also be used, including silanes, dimethylzinc, hydrogen sulphide and hydrogen selenide.

Because only minute amounts of the dopants are actually deposited on the substrate to form the micro-circuits, the majority of the reactants leave the reactor as vent gas and generally require abatement before release. In addition to the main release stream containing excess reactants, there is usually a second stream from the vacuum system tused to creates the low working pressure.

Waste dopant gases containing arsine or phosphine can be abated by scrubbing with an oxidising agent such as sodium hypochlorite solution or acidified iodate or bromate solutions. Soluble salts form and remain in solution. Activated carbon is used to control a variety of pollutants - including those from epitaxial deposition processes - and incineration systems have also been used.

2.1.15.3.3 Related semiconductor activities

Certain micro-circuit deposition operations are carried out using other reactor techniques, usually involving ion implantation or molecular beam methods, and they are used primarily where the substrate is a silicon wafer and the product is a tailored integrated circuit. These processes use and release significantly smaller quantities of arsine and phosphine reactants than the deposition processes described above, but they may generate in the reactor some significant gaseous breakdown products, particularly if a plasma-enhanced technique is involved. Some of these compounds are toxic and polluting so suitable abatement is a normal requirement.

Processes associated with micro-circuit production include acid and solvent etching, metallisation and cutting into smaller sections. These are all carried out in clean-rooms and may involve the use of perfluorocarbons (PFCs) or other perfluorinated compounds, all of which have high global warming potential and most of which are included in the Kyoto list of substances.

Because only minute amounts of the dopants are actually deposited on the substrate to form the micro-circuits, the majority of the reactants leave the reactor as vent gas and generally require abatement before release. In addition to the main release stream containing excess reactants, there is usually a second stream from the vacuum system used to create the low working pressure.

2.1.15.3.4 Release routes from compound semiconductor activities

Emissions to air

- Particulate matter and gaseous compounds, including metalloids and their compounds like arsine, phosphine and silane. These may be oxidised during abatement.
- VOCs including chlorinated and fluorinated hydrocarbons, and other perfluorinated gases.

Emissions to water

- Liquids from wet abatement processes used for gaseous and particulate matter abatement, after suitable treatment.
- Spent acids from etching processes used in micro-circuit production, after pH adjustment.

Emissions to land

- Spent filter units and carbon cartridges.
- Waste acid and solvent etchants may have to be disposed of off-site.
- Solids produced by treatment of aqeous releases.

2.1.16 Activities involving Cadmium or Mercury

The Inorganics PPC sector includes activities that were regulated under IPC as manufacturing activities involving the use of cadmium or mercury or their compounds which may result into the release into air of any of those substances, and it also covers the recovery of compounds of cadmium or mercury.

Smaller **cadmium plating** operations fall within this sector but technical guidance for cadmium plaing activities is included in the guidance note for Surface Treatment of Metals and Plastics, IPPC S2.07 (**Ref 23**).

The manufacture of **nickel-cadmium (Ni-Cad) batteries** would fall within this sector (providing that there is the potential for release of cadmium or its compounds to air) but it is understood that there is no manufacture of Ni-Cad batteries in the UK so no guidance for this activity is provided in this Note.

2.1.16.1 Cadmium pigment manufacture

The Marketing and Use Directive and consequential UK legislation severely restrict the sale and use of cadmium-containing materials. The exceptions are generally safety -critical applications and in the case of pigments for plastics its use is mainly in safety-related applications.

2.1.16.1.1 Cadmium pigment production

Cadmium metal is heated in a gas flame in the presence of air to produce cadmium oxide, which is collected in fabric filters. A secondary-stage HEPA filter reduces the exhaust air content to acceptable levels and maximises cadmium oxide recovery. The oxide is converted to the respective sulphate by the addition of sulphuric acid - or, alternatively, the sulphate can be generated directly by dissolving the cadmium metal in sulphuric acid.

Cadmium sulphide (or, sometimes, cadmium carbonate) pigment is precipitated from the sulphate solution by the addition of sodium sulphide (or sodium carbonate), with the actual shade of colour being determined by the simultaneous addition of zinc or selenium compounds during the precipitation stage. The precipitate is separated by filtration and the cake acid-washed to remove any sodium sulphate before being dried and then calcined at 540-610°C to change the crystal structure to yield a pigment of the required colour. The calcined product is acid-washed again and then dried to remove any free cadmium or its oxide. Finally, the pigments are milled and blended to obtain the required grade of final product for packing.

Local extract ventilation systems exhaust to air through fabric filters.

2.1.16.1.2 Releases from cadmium pigment manufacture

Emissions to air

- Cadmium oxide fume released during the cadmium oxidation stage, abated by HEPA filters.
- Cadmium sulphide released during the drying stage and final product packing, abated by HEPA filters.
- Sulphur dioxide during calcining, abated by alkaline wet scrubbing.

Emissions to water

- Acid-wash liquors from the precipitation stage, which may contain cadmium.

Emissions to land

- Filter dusts, floor sweepings and effluent sludges containing appreciable quantities of cadmium; generally suitable for recycle or recovery so disposal not normally required.
- Minor contaminated consumable materials; generally suitable for landfill.

2.1.16.2 Cadmium glazing

Cadmium pigments can be used within the pottery industry to obtain bright red, orange and yellow glazes. The glaze is applied as a suspension, and any excess is removed before the pottery passes to the furnace for firing.

2.1.16.2.1 Releases from cadmium glazing operations

Emissions to air

- Heavy metals (including cadmium) and volatile organic chemicals during firing.

Emissions to water

- Cadmium from cleaning during glaze application - but the quantities should be negligible as the whole area should be segregated and all wash or cleaning waters collected. Solids should be separated off and the water recycled so that the process has zero discharge to water.

Emissions to land

- Damaged pottery and other contaminated solid waste containing cadmium pigment. (All solids separated from wash waters should be returned for cadmium recovery.)

2.1.16.3 Control of cadmium emissions

2.1.16.3.1 Emissions of cadmium to air

Cadmium-containing particulates and fume should be contained for recycle or recovery but because of the particle size usually found in cadmium-laden fumes (and the requirement for very low ELVs for release of cadmium to atmosphere) cyclones and electrostatic precipitators are not likely to be effective.

HEPA filters are able to remove sub-micron particles and emission levels of cadmium of less than 0.05 mg/ Nm^3 are readily achievable, so fabric filters backed up by HEPA filters are generally regarded as BAT for most cadmium processes.

2.1.16.3.2 Aqueous emissions of cadmium

Aqueous streams containing cadmium should always be segregated where practicable, with a view to recycling the stream. Some processes (e.g. electro-plating with cadmium cyanide, and ceramic glazing) use techniques to segregate, treat and completely recycle aqueous streams containing cadmium, and aqueous releases are effectively zero or are minor and occasional (e.g. from treated ion-exchange regeneration solutions). Only cadmium-contaminated wastes or recovered materials that cannot be re-used should be sent for disposal.

(a) Cadmium hydroxide precipitation

Hydroxide precipitation is the most common technique used to remove cadmium from aqueous streams and, after settling the precipitate, the solution is often filtered to remove any remaining solids. The settled sludge can be concentrated in a decanter centrifuge or filter press to obtain a sludge with a solids content of 35% which, if reasonably free of other heavy metals, is suitable for recovery of cadmium.

Cadmium hydroxide has a low but significant solubility and, with the simultaneous difficulty in filtering out all the fine precipitate, hydroxide precipitation on its own cannot reach the low levels achievable by other techniques so if there is to be a discharged stream, further treatment is usually required (e.g. sulphide precipitation and/ or membrane filtration).

Hydroxide solubility for most metals varies significantly with pH and optimum conditions are essential for effective cadmium removal. At pH 11.4 cadmium hydroxide has its minimum solubility (0.05 mg/ l as cadmium) but at pH 9 it is 0.8 mg/ l, and at higher pHs complex species are formed and the solubility starts to rise. On plants where several heavy metals are present in the effluent stream, it is not uncommon to use pH 9-9.5 as this is the optimum for overall heavy-metal precipitation, as well as being within the normal trade effluent consent limit of pH 10 max - but it is not acceptable for streams containing cadmium.

Cadmium hydroxide precipitation should therefore be operated at pH 11-11.5 - but even at this pH, the solubility can be affected by initial concentration, the presence of other heavy metals and the presence of chelating agents, particularly EDTA, which can increase cadmium hydroxide solubility dramatically.

(b) Cadmium sulphide precipitation

Sulphide precipitation is more effective than hydroxide precipitation because cadmium sulphide is very much less soluble than cadmium hydroxide. At and above pH 9, and in the absence of other heavy metals and chelating agents, the solubility of cadmium sulphide is less than 0.05 mg/ l (as cadmium).

After cyanide destruction (if required) and pH adjustment, sulphide is added in the form of sodium sulphide, sodium hydrogen sulphide or iron sulphide. Sodium sulphides are readily water-soluble (154 g/1) and cadmium sulphide is readily precipitated out - but careful control is required to ensure that there is no significant excess of sodium sulphide in the final stream which could release highly toxic and malodorous hydrogen sulphide if it became acidified.

Iron sulphide is only sparingly water-soluble (5 mg/ l) and the problem of significant excess sulphide being present in the final effluent is generally avoided, but due to its low solubility the effluent treatment system has to be designed for very long residence time to ensure maximum cadmium sulphide precipitation.

As with the hydroxide, the difficulty in removing the fine cadmium sulphide particles by filtration means that sulphide precipitation coupled with a simple filtration technique is also unlikely on its own to achieve benchmark emission levels.

(c) Cadmium carbonate precipitation

Carbonate precipitation is brought about by the addition of sodium carbonate at pH 9 - 9.5. The solubility of cadmium carbonate is 0.1 mg/ l (as cadmium) but levels of 0.06 mg/ l are often achieved, it is thought as a result of sorption of cadmium on to the metal carbonate precipitate.

The removal of the precipitate from the effluent stream is the same as that used for hydroxide and sulphide precipitation and, like them, a further stage of treatment is likely to be required to achieve the benchmark emission level.

(d) Electrochemical removal of cadmium

Electrochemical systems for cadmium removal have been developed and are available commercially. They utilise electrochemical techniques to remove Cd $^{2+}$ ions from recirculating potential effluent streams and plate it on to a cathode. In the plating industry this cathode can then be used as the anode for cadmium electroplating.

(e) Membrane processes for cadmium removal

Membrane processes - micro-filtration, ultra-fitration and reverse osmosis - can all polish the solutions from precipitation or other primary treatments to achieve benchmark release levels for cadmium.

2.1.16.4 Use of mercury or its compounds

Although declining in use generally, mercury retains a number of essential applications. In elemental form it is used in a variety of equipment and instruments, including fluorescent lamps, manometers and thermometers, electrical control and switching systems, AC-DC rectifiers and gas-filled valves, and certain vacuum pumps. These manufacturing processes typically involve the filling of a specified quantity of mercury (ranging from a few milligrams to hundreds of grams) into the device, which is then sealed to retain the mercury.

2.1.16.4.1 Manufacture of mercury compounds

The manufacture of mercury compounds has declined very significantly as a result of legislation prohibiting their use in many areas (e.g. plant protection), and where there are non-prohibited uses, the majority of compounds still in use in the UK are imported. A limited number of mercury compounds are produced in small quantities for specialist requirements, and these are typically manufactured using conventional small batch reactor techniques.

2.1.16.4.2 Manufacture of mercury fluorescent lamps

Mercury is used in the mass production of most discharge lamps worldwide. Mercury has a high vapour pressure at ambient temperatures and it has a high efficiency of luminosity versus power consumed for white light applications. When excited electrically the mercury atoms emit blue-green and ultraviolet radiation, and the latter then excites the phosphor coatings of the lamp to emit red-yellow light and provide a more balanced output approaching that of white light.

Low-pressure tubular discharge lamps typically contain 10-20 mg of mercury which is all available as vapour when the lamp is new, but which gradually reacts with the lamp internals until there is insufficient vapour to complete a discharge circuit. This can determine the life of the lamp, so it constrains developments to reduce the amount of mercury used per lamp - though in the newer smaller devices the mercury inventory has been reduced to 6 mg or less.

Plant manufacturing low pressure devices mass-produce specific products on a number of dedicated lines, usually using the manufacturer's own detailed technology. A typical process line for conventional tubes is as outlined below:

- Glass tubes and lamps are machine washed, coated, dried and baked, and a cathode assembly is sealed by flaming.
- The assembly is fed to an exhauster machine, which is a multi-port carousel arrangement ndexed to to a number of staged operations. The first stage is evacuation, an inert gas is introduced and the cathode is energised to activate it.

- The lamp is heated to complete the drying of the coating, re-evacuated and recharged with inert gas at the required low working pressure.
- A metered droplet of liquid mercury is injected from a dispenser and the lamp is sealed by flaming. Pure mercury (99.999%) is required for satisfactory lamp performance, and this may be bought in as 'triple-distilled' mercury or it may be redistilled by the lamp manufacturer (as may any mercury recovered from exhauster dispensers removed for maintenance, etc).
- The lamp is then energised and any that fail to light or to remain lit are automatically ejected.

To eliminate the release to air of mercury from the vacuum system, other methods of loading mercury into lamps have been developed which encapsulate the mercury until after the lamp has been sealed. These might be considered to be BAT for new installations but a major investment in process and product verification is likely to be required for the conversion of an existing plant to such a system.

High-pressure fluorescent discharge lamps are made for commercial use on a much smaller scale than low-pressure lamps - and they generally use techniques that inject the mercury into a sealed lamp, and thus should avoid release of mercury to air.

2.1.16.4.3 Mercury instruments and control/switching devices

The filling of instruments and control/ switching devices with elemental mercury is declining, but still takes place in diverse processes and in quantities ranging from a few specialist items per month to thousands of consumer items per month. Examples include thermostats, mercury-in-glass and mercury- in-steel thermometers, and manometers.

The most likely sources of emissions are the exhausts from vacuum systems and from local ventilation systems.

2.1.16.4.4 Release routes from mercury manufacturing activities

Emissions to air

- Mercury vapour drawn into vacuum systems and then expelled directly to air or into local exhaust ventilationsystems.

Emissions to water

- In most situations, no release to water should occur.

Emissions to land

- Rejected or broken filled products where it is not practicable to recover the mercury.
- Waste vacuum pump oil contaminated with mercury, arising from regular oil changes. In addition, pumps returned to the suppliers for overhaul will give rise to similar waste.

2.2 Emissions control

2.2.1 Point source emissions to air

The nature and source of the emissions expected from each activity is given in previous sections and should be confirmed in detail in the emissions inventory of the Application for a PPC Permit.

A wide variety of techniques are available for the control of releases to air, and the BREF on Common Waste Water and Waste Gas Treatment/ Management Systems in the Chemical Sector (see **Ref 1**) should be consulted. Section 3.5 of the BREF has details of available air abatement techniques and Section 4.3.2 contains recommendations on what might constitute BAT for a variety of abatement techniques for releases to air.

For a diverse sector like Inorganic Chemicals, none of the abatement techniques described in the following sub-sections for controlling emissions to air can be described as BAT for all situations; the particular circumstances of the installation will affect assessments of which is best. Vent streams have a wide range of properties that can influence the choice of abatement technique, such as:

- have high or varying flow-rate (with or without a major inerts content);
- are at high temperature;
- are laden with particulates;
- are odorous;
- are "wet" or near saturation; and
- comprise mixtures of components such as corrosive, toxic or flammable gases, VOCs, metal/metal compound vapours or dusts, or combustion products (NO_X, SOx).

In addition to the inherent properties of the exhaust gas, other factors such as the following will also determine which techniques are BAT for a specific installation:

- Desired quality of the final emission to air (i.e. ELVs, particle size, visibility, residual odour);
- Capital and operating cost;
- Specific plant layout, and availability of utilities and recovery options.

Often a combination of techniques is required to abate emissions but there are some general requirements which should be considered as being part of BAT for control of emissions to air from point sources, and these are included in the following BAT box.

Indicative BAT requirements for the control of point-source emissions to air (Sheet 1 of 2)

1 In conjunction with information in this Guidance Note and relevant equivalent sections in the Guidance Notes for the Organics sector, information and recommendations in the BREF on Common Waste Water and Waste Gas Treatment/ Management Systems in the Chemical Sector (see **Ref 1**) should be formally considered as part of the assessment of BAT for point-source releases to air.

2 The benchmark values for point source emissions to air listed in **Section 3.2.1** should be achieved unless alternative values are justified and agreed with the Regulator.

3 The main chemical constituents of the emissions should be identified, including VOC and particulates speciation where practicable.

Indicative BAT requirements for the control of point-source emissions to air (Sheet 2 of 2)

4 Vent and chimney heights should be assessed for dispersion capability and an assessment made of the fate of the substances emitted to the environment (see **Section 4**).

Control of visible particulate plumes

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

Control of visible condensed water plumes

6 The need to minimise water vapour plumes should always be considered as, in addition to possible local visual amenity issues, in severe cases, plumes can cause loss of light, fogging, icing of roads, etc. High moisture content can also adversely affect plume dispersion so, where practicable, water content of the exhaust stream should be reduced. Ideally, the exhaust should be discharged at conditions of temperature and moisture content that avoid saturation under a wide range of meteorological conditions, including cold damp conditions.

7 The use of **primary energy** to reduce a plume simply because it is visible is not considered BAT. However, it may be appropriate to use **waste or recovered heat**, for example, heat in a gas stream prior to wet scrubbing can be used for re-heating the exhaust stream after scrubbing by means of a gas-gas heat exchanger. The use of energy for exhaust gas re-heat should be balanced against the benefits gained.

8 For cooling towers, plume abatement may be achieved by combining conductive heat exchange and evaporative cooling in the design of the tower. The degree of abatement required will depend upon local conditions and the distance from the towers to the nearest sensitive area. Plume modelling should be employed by an applicant to confirm that the visible (condensed) plume will not ground beyond the boundary fence nor reach areas of habitation at a height that will cause significant loss of light. As a guide, the width of the plume should not fill an arc which subtends an angle greater than 10° when viewed vertically from the ground.

Abatement techniques for the following types of emission are discussed in the sections below:

- Particulates and dust;
- Gaseous pollutants.

Control of volatile organic compounds (VOCs) is described in detail in Section 2.2.1.1 of the Speciality Organic Chemicals sector guidance, S4.02, (see **Ref 23**) and that Note should be consulted where VOC emissions are significant.

2.2.1.1 Particulate and dust abatement techniques

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

Further information is available in the Waste Water and Waste Gas treatment BREF (**Ref 1**).

2.2.1.1.1 Cyclones

Cyclones are the principal type of gas-solids separator employing centrifugal force, and are widely used. They are particularly effective for the removal of particles with a diameter >10 microns and are often used as a secondary device for the protection of more expensive abatement equipment that can achieve better release levels, i.e. as the first stage in a multi-stage particulate abatement system.

There are two basic types of cyclone - reverse flow and straight through - differentiated by the geometry with which the gas stream enters the cyclone. They can be manufactured from a wide range of materials; and can be designed for both high-temperature and high-pressure operation.

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

Cyclones are often used as the primary or f In other circumstances they can be irrigated to reduce levels of dust re-entrainment.

Inertial filters

A newer concept in particulate removal - the inertial filter - claims to achieve high removal efficiency by the use of an impeller that is rotated at speed within the cyclone enclosure. Dust-laden air from the process enters the enclosure and the larger particles drop out into a collection silo. The smaller, less dense particles follow the gas flow towards the spinning impeller. On approaching the spinning impeller, these smaller particles accelerate in the plane of the rotating blade and separate from the air flow. This dynamic barrier inhibits the passing through of particulates and the efficiency of separation can be modified by changing the speed of the impeller.

2.2.1.1.2 Fabric Filters

Fabric filters are widely used for the collection of particulates >1 micron and can usually achieve efficiencies of greater than 99%. They are particularly useful as secondary or tertiary gas cleaning devices following a cyclone, dry scrubber or fluidised- bed absorber located upstream.

However, although fabric filter design improvements such as inlet technology, off-line cleaning and advanced fabrics have resulted in very high collection efficiency being achievable even with fine particles, fabric filters have their limitations. Particulates <1 micron in diameter (e.g. metal fume) will require fabric filters to be backed up by, or replaced by, other devices such as HEPA filters (see **Section 2.2.1.1.3** below). An example of this is in the production of red lead where fabric filters are followed by HEPA filters (following initial dust removal in a cyclone).

The industrial fabric filter is generally constructed from a woven material or a felted fabric to provide the filtration medium through which the particle-laden gases are passed. Filtration efficiency can often be enhanced by pre-coating the filter cloth prior to use, but fabric filters are not generally suitable for moisture-laden streams or those with tarry or sticky characteristics owing to adherence leading to "blinding" of the fabric. Fabric filters can cope with a wide range of substances and operating conditions but ceramic cartridge filters are generally better where there are very high temperatures or large, rapid temperature changes.

Fabric filers are available in cartridge form as well as bags. Cartridges tend to be of smaller size but have a larger filtration area than bags designed for the same duty, and are often more efficient filters.

Where reasonable and practicable, the performance of fabric filters should be monitored by measuring the dust concentrations upstream of the filters as well as in the exhaust stream. Procedures should be in place to ensure filters are cleaned before operating efficiency is compromised by excessive build-up of captured particulates, and bag failure should be indicated and alarmed by, say, the use of an opacity meter or particle impingement detector, or by appropriate pressure-drop monitoring.

Apart from the choice of fabric for the filter medium, the required particulate removal efficiency is only maintained by routine cleaning and maintenance of the filters - as described below:

Fabric filter types

A number of fabrics are available to deal with the wide range of temperatures, corrosiveness, composition, particle size, etc, and the more important fabrics that are used as filter media are shown in **Table 2.5**.

Table 2.5: 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
Goretex	Polytetrafluoroethylene (PTFE)	Excellent	Excellent	230	260	Poor
Dralon T	Homopolymer acrylic	Good	Excellent	140		Poor
Bekipor	Stainless steel	Good	Good	454	538	Good

Filter cleaning mechanisms

As particles build up on the surface of the filter initially they aid the filtration mechanism but eventually the pressure-drop increases in parts of the filter to the point where overall removal efficiency falls and/or gas throughput is restricted. To address this problem fabric filters are usually fitted with automatic cleaning mechanisms that periodically remove the bulk of collected material, and the 3 main types can be summarised as:

- shaker – where the filter bags are shaken to dislodge the particulates;
- pulse jet – where a pulse of compressed air is applied in the reverse direction to the normal flow;
- reverse flow – where clean air is passed through the filter in the reverse direction to the normal flow.

Some pulse-jet units have variable blowing sequences for filter-bag cleaning and the frequency of jet pulsing can be controlled by the pressure-drop across the filter element so that bag cleaning cycles can be set to match filtration load. This not only maintains optimal particulates removal but avoids the use of excessive compressed air and shortened bag life, which can result from excessive cleaning cycles.

Where continuous operation is necessary and filters have to be taken off-ine for cleaning, to maintain the required standard of particulate abatement a multi-filter system which allows cleaning to take place whilst at least one filter is left on-line, should be used.

2.2.1.1.3 High-efficiency particle arresters (HEPA filters)

HEPA filters generally contain a filtration medium consisting of a bed of densely packed fibres (often spun-bonded polymers) or sintered material. Owing to the density of packing and the type and thickness of the fibres, HEPA filters are capable of achieving high removal efficiencies for particles of 0.5 micron diameter and larger - and they can also remove a significant proportion of particles down to 0.01micron diameter.

Like fabric filters, HEPA filters are not generally suitable for use in moisture-laden potentially sticky streams due to the adverse effects of 'blinding', and the condition of HEPA filters and their performance can, and should, be monitored by similar methods to those used for fabric filters.

HEPA filters have the disadvantage of high pressure drop and can therefore be unsuitable for large airflows where the required size of filter leads to comparatively high capital and operating costs.

Self-cleaning versions use a reverse air pulse system similar in principle to fabric and ceramic filters.

2.2.1.1.4 Ceramic Filters

Ceramic filters are constructed in two basic varieties: high-density and low-density. The high-density units generally comprises a silicon carbide base supporting a fine coating (usually aluminium silicate); the low-density units usually comprises matted mixtures of silica and alumina fibres. However, they may also be constructed from other materials, such as metal "fibres", sintered metal or granulated activated carbon cloths.- and an example of a more robust filter is an all-metal filter with a sintered nickel membrane incorporated into a stainless steel housing.

Filtration efficiencies >99.9% for particles of 1 micron size are attainable. The high-density units have a higher pressure drop than the lower density type, but both have high temperature capability with some materials capable of withstanding temperatures of 1000 ºC, rapid temperature shock from 900ºC to 0ºC, and frequent thermal cycling. Cleaning and regeneration is achieved by reverse air pulse jet, an operation similar to that undertaken with bag filters

Ceramic filters can be used for "dry scrubbing" of acid gases and heavy metals where reactant or adsorbent solids such as calcium carbonate, calcium oxide or calcium hydroxide are injected upstream of the filter.

2.2.1.1.5 Electrostatic precipitators

Electrostatic precipitators (ESPs) 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.

There are two main types of ESP - wet and dry - and both can achieve very high collection efficiencies of dust or fume particles down to 0.01 micron diameter. They can operate at high temperature (up to 450ºC) and, unlike bag filters, at high humidity. ESPs may be preceded by a conditioning tower to improve performance, and can be designed for low pressure drop and therefore lower power requirement for induced draught. Compact units are available for small applications.

The disadvantage of ESPs is the inherent risk of sparking off explosions of flammable gas mixtures. This limits the application of electrostatic precipitators, particularly for processes using flammable organic solvents, and great care needs to be taken where there is the possibility of generating flammable concentrations of substances like carbon monoxide.

Turbulent precipitator - A relatively novel filter, known as a turbulent precipitator, has been developed in which particulate-laden air is passed over the filter medium generating a static charge, which attracts and holds dust particles. This unit can be used for very hot gases, and for the removal of either fine solid or liquid particles from gas streams. It has many similarities to an electrostatic precipitator but does not require electricity.

2.2.1.1.6 Wet collection (scrubber) devices

Scrubbing operates on the principle that particulates can be removed from gas streams by dissipating their momentum, either by impacting the particulate directly on to the scrubbing liquid or by impacting a solid surface, which is then washed by irrigation. Scrubbing systems tend to be less effective than other alternatives for the control of particles <10 micron in diameter, and they are not so good where mists can be formed. They also generate an effluent stream that will require treatment, but they have a relatively constant pressure drop, do not present secondary dust problems and are versatile, i.e. they can handle high-temperature gas streams, moisture-laden gas streams, corrosive gases and aerosols.

Wet collection devices use a variety of methods to wet the particles to remove them from a gas stream but the main techniques for contacting the scrubbing liquid with the gas stream are broadly similar to those used for absorption of, say, acid gases or VOCs. The technologies available vary in terms of cost, collection efficiency and energy requirements - with increased energy input resulting in increased removal of particulate matter. They include venturi, jet, dynamic, centrifugal and impingement scrubbers, but generally only the venturi and jet scrubbers are suitable for sub-micron particles.

In a venturi scrubber the gases are drawn into the throat of a venturi tube to which pressurised water or absorbent solution is injected. Particle size collection efficiency is a function of pressure drop and at the lower end of the range (250 mm water-gauge) removal of particles of a few micron in diameter is practicable. However, for sub-micron particles pressure-drops at the upper end of the range (1500 mm water gauge) may be required, particularly where >99% collection efficiencies are required.

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

2.2.1.1.7 Dust suppression equipment

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

2.2.1.2 Gaseous pollutant abatement techniques

There are many methods available for reducing and minimising discharges of gaseous pollutants in emissions to atmosphere. Some of the main types are as follows:

- absorption - (packed and plate tower scrubbers, spray towers, wet mop scrubbers and rotaclones);

- condensation;
- thermal decomposition - (thermal incineration, catalytic incineration, flares);
- adsorption - (activated carbon).

Absorption is probably the technique most likely to be encountered in the Inorganic chemicals sector, but other techniques, including some not mentioned here, may be more appropriate.

The removal of VOCs is covered in some detail in Section 2.2 of both Organics sector guidance notes, S4.01 and S4.02 (see **Ref 23**) so some of the techniques that can be used for removal of VOCs have not been reproduced below.

2.2.1.2.1 Absorption

Absorption is the most common method for the removal of soluble components of a gas stream. The absorbent or scrubber liquor can be water, acid or alkali neutralising solution or suspension, or an oxidising or reducing agent according to the nature of the substance to be removed. It can also be an organic compound for absorbing VOCs or a specialist absorption agent that is selective for the substance to be removed. The absorbent is usually recirculated round the absorber and its concentration maintained at an effective level by bleeding-off a proportion for recovery or disposal, and making up the volume with fresh absorbent.

To achieve optimum mass transfer of the pollutant from the gas phase to the liquid phase, there should be:

- ready solubility of the pollutant in the absorbent at all levels in the absorber;
- maximum interfacial contact (i.e. wetted surface area) between gas and liquid phases; and
- sufficient residence time for absorption.

The most common arrangement - the one with the highest theoretical mass transfer - has the vent gas flowing counter-currently to the absorbent liquid so that the most dilute gas is contacted with the most concentrated absorbing liquor, and the concentration difference is maximised for the entire length of the scrubber.

Consideration should always be given to using an absorbent that can be used in the same process, for example by using an appropriate raw material or solvent as the absorbent to recover raw materials, solvent or products for direct recycled to the process - or, alternatively, used elsewhere (e.g. using water to absorb hydrogen chloride or other acid gases such that the resultant acid is of sufficient strength to be used as a raw material or for effluent treatment). In most of these cases, two or three absorbers in series will be required, with the final scrubber operating at a concentration and temperature designed solely for minimising the release. In the case of volatile organic solvents, absorption into non-volatile oil is a very effective technique for removing and then recovering the solvent, especially halogenated organic solvents such as dichloromethane.

In all absorption systems, sufficient instrumentation and alarms should be installed to ensure that liquid level and flowrate are maintained and that temperatures and pressures are within be monitored frequently if not continuously, and directly if not via reliable surrogate parameters. Scrubbers should include sample points upstream as well as downstream to allow analysis of inlet gas as well as monitoring of the gas exiting via a plant stack to atmosphere.

In absorption abatement, a potential release to air is often transferred to a potential release to water or land, and the absorbent itself may require further treatment. However, absorption is often BAT, particularly where the process concentrates the pollutant into the absorbent and makes it available for recovery for re-use or sale, or provides for easy disposal. In the case of solvents or VOCs in vent streams, a standard process uses a combination of absorption into a liquid stream, distillation of the “spent” absorbent, and condensation to recover the solvent or VOC in a usable form.

Packed and Plate Tower Scrubbers

In a packed tower scrubber the packing material provides a large surface area for mass transfer between liquid and gas phases. In the plate column the plate disperses the gas into numerous bubbles to create a similar large surface area for mass transfer. Even distribution of scrubbing liquor and prevention of plugging or channel flow is of critical importance to the satisfactory operation, particularly in plate designs.

The advantages of packed tower scrubbers include modest to low pressure drops, ease of construction with chemically resistant material and a very wide choice of packing geometries and materials of construction.

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

A variation on the packed tower design which gives high-efficiency gas scrubbing is based on a fluidised-bed design. High turbulence is caused by fluidising the packing bringing the counter-current gas and liquid streams into intimate contact, significantly enhancing the mass transfer characteristics of the system. Reductions in the height and diameter of the system can be achieved, and the system can remove particulates without encountering the conventional solids blockage problems of a packed tower system.

Spray Towers

Spray towers can achieve good removal rates where the pollutants are very soluble in the absorbent. Mass transfer is achieved by atomising the absorbent with nozzles and may be enhanced by the use of appropriate surfactants.

The advantages of these units are relative cheapness as a result of their simple design, easy construction in corrosion-resistant material and ease of maintenance, and low energy requirements due to low pressure drop. However, nozzles can become worn or clogged fairly easily, particularly if the gaseous stream contains particulates.

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

Wet-Mop Scrubbers and Rotaclones

In wet-mop scrubbers, absorbent is injected into the impeller casing where it is atomised and mixes with the extracted air stream. The impeller is usually of a wettable and flexible fibrous material. The exhaust stream then passes to a demister, and the recovered absorbent is either discharged to drain or recirculated to the wet-mop scrubber.

Rotaclones are similar to wet-mop scrubbers but the impeller is rigid. Rotaclones tend to be used for high air flowrates, wet-mop scrubbers for lower ones.

2.2.1.2.2 Thermal or catalytic decomposition

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

Four basic decomposition processes can be employed - thermal incinerators, catalytic incinerators, flameless oxidisers and flares - and in certain circumstances the waste gases can be fed through process boilers or heaters. In all cases, sampling points should be in place for monitoring the performance of the combustion process and several parameters should be continuously monitored.

Apart from flame failure, combustion temperature and pressure, these could include monitoring for oxygen, CO, particulates and specific substances which demonstrate the effectiveness of the abatement technique.

In the Inorganics sector, use of these techniques is relatively limited but they are utilised in specific applications, e.g. the removal of low concentrations of hydrogen sulphide. Where they are used, considerable fuel savings can be realised by use of heat exchange systems before and after the oxidation stage - and the following techniques are in common use in the chemical sector as a whole:

- Recuperative - heat transfer between the exit gas and the incoming vent stream; up to 70% of the energy in the exit gas may recovered.
- Regenerative - use of a direct-contact ceramic exchanger which, alternately, is heated by exit gas and then switched over to heat the incoming cold vent gas; this cyclic process can provide very high energy recovery (up to 95%).
- Conventional energy recovery - additional heat exchangers can recover energy as steam or hot water.

Thermal Incineration

Thermal incinerators are used to control waste gases containing low concentration of pollutants. For example, waste gases containing arsine gas and other arsenic compounds in hydrogen carrier gas from semiconductor manufacturing operations can be controlled by thermal incineration.

The temperature of the incinerator, oxygen concentration and the gas residence time are the most important operational variables. The calorific value of constituents in waste streams varies so a support fuel is normally required to maintain the desired temperature. Reference should be made to the Waste Incineration sector guidance, S5.01, (see **Ref 23**) for information on achievable emission levels.

Catalytic Incineration

Catalytic incinerators employ a bed of active catalyst material to facilitate the oxidation reaction to take place at a lower temperature (typically 150 - 500°C) and at a faster rate than in a thermal incinerator, but the gas flow rate and the concentration of combustibles have to be kept fairly constant for optimal performance. Furthermore, catalytic oxidisers tend to be less robust than thermal oxidisers, and waste streams containing particulate matter often cannot be destroyed effectively if the particulates have a tendency to blind the catalyst surface. Similarly, catalytic oxidisers are sensitive to gaseous constituents in the waste gas, but poison-tolerant catalysts are available for the removal of hydrogen sulphide, hydrogen cyanide and chlorinated organics.

Specialist systems have been developed for particular applications and proprietary catalytic cartridge columns have been successfully used to abate hydride gases from ion-implantation-type semiconductor processes.

All catalysts deteriorate with use and need to be replaced periodically, so the performance should be monitored regularly so that deterioration is noted at an early stage and remedial action taken. Many catalysts include precious metals or other metals so if return to the manufacturer for regeneration is not an option, a satisfactory disposal route has to be identified..

Flameless Thermal Oxidisers

Flameless oxidisers allow oxidation at reduced temperature by passing the waste gas through a preheated ceramic packing - and in the absence of a high-temperature flame, formation of NO_X is lower. A similar effect may be achieved in a regenerative system operating under auto-thermal conditions.

Flares

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

Flare systems should be designed to internationally-recognised standards to allow combustion of all gases necessarily vented to it under all circumstances, with justification for the anticipated worst-case scenario and the chosen flare height. The effect of low and varying gas-flows and the consequences of wind dilution should be allowed for in the design, and flares should burn without smoke under all conditions. Knock-out pots or drums should be installed as close as practicable to the flare to catch liquids and condensible material.

Problems associated with flare systems include:

- The heat generated may be unacceptable without careful design;
- The light and luminescence of the flame may be a nuisance if the plant is near an urban settlement, and concealed combustion chambers or ground flares should be considered in such cases;
- Flare-tip mixing systems can cause increased noise levels;
- Incomplete combustion can result in the emission of toxic or noxious substances;
- Both oxygen-starved and over-oxygenated flames can result in the emissions of toxic or noxious substances;
- Flaring of halogenated substances should be avoided
- Flares need to be kept lit constantly with a robust pilot light, and flame-failure alarms should be installed on pilot lights;
- Constant purging is generally required, and
- Monitoring of emissions from flares is generally impracticable so it is difficult to ensure complete combustion.

Neither the intrinsic value nor the thermal value of the gas can be recovered if it is flared, so to minimise flaring flare-gas recovery systems should be considered.

2.2.1.2.3 Adsorption

Adsorption describes the removal of gaseous components from a gas stream by adherence to the surface of a solid (the adsorbent), the most common of which are activated carbon, silica gel, activated alumina and zeolites.

The polarity of the surface of the adsorbent determines the type of vapours for which the adsorbent has the greatest affinity. All but activated carbon in the list above are polar adsorbents, and polar adsorbents tend to adsorb water vapour preferentially so if moisture is present in the gas stream, their application to pollutant removal is limited. Activated carbon is the only common non-polar adsorbent and it is s used to control emissions of organic solvents, odours, toxic gases, acid vapours, phenols and hydrocarbon vapours.

The following sections concentrate on activated carbon systems.

Activated carbon absorption

Carbon adsorption systems can be of fixed-bed or rotary wheel design and be regenerative or non-regenerative. In all cases the vent gas stream should be pre-treated to remove any particulate matter or entrained liquids and then, in most cases, the gas is passed downwards through the carbon bed to reduce the entrainment of carbon particles in the exhaust gas. High humidity can also interfere with the adsorption process and humidity levels can be reduced by cooling to condense out water vapour and then re-heating the gas back to its original temperature.

Fixed-bed, regenerative systems usually take the form of two or three beds operating in parallel, with one on-line, one regenerating and, in the case of three beds, one on stand by - with pipe-work designed for simple and efficient changeover between beds. A variation of this multiple-bed system sees two carbon beds in series, with changeover between the two beds being initiated when breakthrough of the first bed occurs.

An alternative to fixed beds is the rotary wheel using a carbon matrix. Vent gas is passed through 90% of the wheel, which is rotating slowly, and the cleaned air passes to the vent stack.By means of a series of specially designed seals, hot regenerating air or gas is passed counter-currently through the other 10% segment and the pollutant desorbed. Such systems are normally employed to concentrate a pollutant stream before passing to an incinerator, and zeolites may be used in place of activated carbon.

Activated carbon adsorption may be used to control releases of metal compounds in gaseous form, for example from semiconductor processes. In these applications, non-regenerating systems are normally used, with the spent cartridge being disposed of to land. The cartridge should be replaced before breakthrough occurs.

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

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

Sample points should be in place for the analysis of inflow as well as exit gas streams and there should be provision for monitoring for breakthrough as well as the crucial operating parameters like temperature and pressure.

Regeneration of carbon beds

Where it is not done continuously, periodic regeneration of the adsorbent bed is required to maintain removal efficiencies. This may be achieved thermally by steam stripping and condensation followed by recovery of the adsorbed material by, in the case of organics, phase-separation or distillation. The aqueous stream may be contaminated and need treatment. An option for regenerating carbon beds which is essentially water-free is to pass hot air that is destined for an incinerator through the carbon bed - though recovery and re-use of the adsorbate is normally the preferred option.

Pressure reduction may also be used to desorb the material from the bed, and in a few cases it may be appropriate to displace the adsorbed substance with a more strongly adsorbed material.

Eventually, carbon loses its ability to be regenerated in situ and it should then be returned to the supplier or a third party for regeneration (in preference to disposal as waste).

2.2.2 Point source emissions to surface water and sewer

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

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

A wide variety of techniques is available for the control of releases to water or sewer, and the BREF on Common Waste Water and Waste Gas Treatment/ Management Systems in the Chemical Sector (see **Ref 1**) should be consulted. Section 3.3 of the BREF has details of available water treatment techniques and Section 4.3.1 contains recommendations on what might constitute BAT for a variety of treatment techniques for releases to water.

In addition to the BREF and the techniques noted below, guidance on cost-effective effluent treatment techniques can be found in **Releases to water references**.

Waste water can arise from the process, rain-water run-off where there is the potential for contamination, from storm water, from cooling water, from treating accidental releases of raw materials, products or waste materials, and from fire-fighting - and, where not insignificant, these should all be taken into account in the Application and in the Permit.

The Inorganic chemicals sector is characterised by enormous variations in waste-water quantity and quality. The effluent streams may contain cyanides, sulphides, dissolved organics, suspended organics, dissolved heavy-metal compounds including sulphates and fluorides, as well as suspended solids. The characteristics of the effluent stream largely depend upon the particular process involved - and this variability has to be taken into account in the selection of minimisation and treatment techniques. The initial definition of all waste-water issues on the installation, not just the composition of the effluent stream, is particularly important.

For a sector like Inorganics, in which almost any known substance could potentially be released, none of the water treatment techniques described in the following sub-sections (Section 2.2.2.1 to 2.2.2.9) can be described as BAT for all situations; the particular circumstances of the installation will effect assessments of which is best. There are however a few general requirements which should be considered as being part of BAT for control of point source emissions to water or sewer, and these are summarised in the following BAT box.

Indicative BAT requirements for effluent treatment and the control of emissions to water

1 In conjunction with information in the following sections of this Guidance Note (Sections 2.2.2.1-2.2.2.9), information and recommendations in the BREF on Common Waste Water and Waste Gas Treatment/ Management Systems in the Chemical Sector (**Ref 1**) should be formally considered as part of the assessment of BAT for point-source releases to surface water or sewer.

2 The following general principles should be applied in sequence to control emissions to water:

- water use should be minimised and wastewater reused or recycled (see also **Section 2.4.3**)
- contamination risk of process or surface water should be minimised (see also **Section 2.2.5**)
- wherever possible, closed loop cooling systems should be used and procedures in place to ensure blow down is minimised
- where any potentially harmful materials are used measures should be taken to prevent them entering the water circuit

3 Consideration should be given to the use of filtration/osmosis or other techniques which allow the effluent water to be cleaned for release or, preferably, for return to the process. Particular consideration should be given to the fate of the concentrated residues of such techniques. These can often be returned to furnaces, evaporated, solidified, sent for incineration etc. Tankering of such residues off the site as waste, simply transfers the problem to another place unless they are sent to a facility with the genuine ability to recycle the materials.

4 If the pollutants in the wastewater are all readily biodegradable or the effluent contains only materials which are naturally occurring in much larger quantities in the receiving water, there may be justification for filtration/osmosis or similar techniques not being considered appropriate.

5 Where prevention is not possible, the emissions benchmarks given in **Section 3**, should be achieved.

6 Where effluent is treated off-site at a sewage treatment works the above factors still apply. In particular, it should be demonstrated:

- the treatment provided at the sewage treatment works is as good as would be achieved if the emission were treated on-site, based on reduction of load (not concentration) of each substance to the receiving water. (The **IPPC Environmental Assessments for BAT - H1 Software tool** will assist in making this assessment.)
- that action plans are appropriate to prevent direct discharge of the waste-waters in the event of sewer bypass, (via storm/emergency overflows or at intermediate sewage pumping stations) - for example, knowing when bypass is occurring, rescheduling activities such as cleaning or even shutting down when bypass is occurring.
- that a suitable monitoring programme is in place for emissions to sewer.

7 There must be an understanding of the main chemical constituents of the treated effluent (including the make-up of the COD and the presence of any substances of particular concern to the aqueous environment). The fate of these chemicals in the environment should be assessed.

8 As a minimum, all emissions should be controlled to avoid a breach of water quality standards (see **Section 3.2** and **Section 4.1**), but where another technique can deliver better results at reasonable cost it will be considered BAT and should be used (see **Section 1.1**). Unless reasonably self-evident, the EQS and BAT points should be demonstrated by calculations and/or modelling in the Application.

2.2.2.1 Effluent minimisation and treatment - Introduction

Waste waters can arise from the process itself, from contaminated rain-water run-off, from storm water, from cooling water, from accidental releases of raw materials, products or wastes, and from fire-fighting - and all of these sources need to be considered in the overall assessment of BAT for emissions to water from the installation.

It is common for the aqueous effluents from several process plants and multiple sources to be treated together, either in a site waste-water treatment system or as a combined stream to external treatment. Sometimes synergistic effects may occur when effluents are mixed; acids and alkalis may neutralise each other, for example, or a dilution effect may be acceptable if it permits a pollutant to be destroyed in a biological system - but often the opposite is true and segregation and separate initial treatment are more effective. The following sub-sections indicate the issues that need to be addressed and options for selecting the best combinations of techniques.

2.2.2.1.1 Identification and definition of waste-water issues

All the waste-water generation sources and subsequent minimisation and treatment issues for a particular installation need to be identified - and the assessment should cover:

- *Site-specific issues.* These can be represented by the use of plans or diagrams for process waste water, surface-water run-off, etc, systems, which show the interactions between the various systems.
- *Characterisation of all waste streams.* In general this should cover the monitoring of the main waste-water streams for flow, pH, temperature, chemical oxygen demand (COD), biochemical oxygen demand (BOD) and potentially toxic or inhibitory pollutants (organic and inorganic).
- *Defining waste-water generation sources and water-use requirements.* This is a necessary step if effluent volumes are to be minimised and the re-use/recycle of water is to be maximised.
- *Listing the chemicals used on the site and any potential contaminants.* This is a general requirement in the Application for a Permit but for the purposes of effluent characterisation, materials which are not routinely released in waste water but which may have a significant impact if entering drains, should be identified and assessed.
- *Worst-case scenarios.* This involves the derivation of potential ‘worst-case’ combinations of flow and loads under routine and non-routine conditions.

Options for improvements in production processes and in waste-stream management should be identified at an early stage and assessed in line with the principles of preventing and minimising pollution as well as making subsequent treatment more effective. Very detailed attention should be paid to preventing releases of substances covered by the requirements of the Dangerous Substances Directive or other statutory arrangements, of pesticides, pharmaceutically-active substances, endocrine disruptors and of other substances identified as being of particular concern.

Two of the main questions to be determined in the quest for the best effluent -stream management system concern:

- *Stream segregation.* Certain waste-water streams may require segregation from the bulk of the process waste water because they are particularly toxic, odorous, non-biodegradable or contain constituents (e.g. solvents) that can be recovered. Examples of streams that should normally be kept separate where practicable are ones contaminated with heavy metals, hydrocarbons, chlorinated hydrocarbons, acids, and alkalis (though the last two are likely to be beneficially combined before final discharge).
- *Stream blending.* Mixing streams may provide nutrients for subsequent biological treatment or optimise pH for metals removal, but blending introduces issues such as:
  - – pH changes may make the resultant stream more corrosive;

  - temperature increases can lead to the liberation of volatiles, and can also facilitate reactions between chemicals that could lead to releases to air;
  - there may be increased potential for adverse microbial or chemical reactions.

2.2.2.1.2 Water use in relation to waste-water management

The understanding of water use has significant implications for the management of waste water; the two are intimately related (“what you don’t use, you don’t have to discharge”) and so require priority consideration by the operator. Techniques for reducing water use include:

- management attitude - to process-unit water metering, targets, audits and publication of appropriate water-use indexes, and to undertaking awareness-raising and training of staff;
- routine leakage checks of water piping, and maintenance where required;
- minimising the presence of water in the process, including water used in purification stages and equipment cleaning (and scheduling of batches to reduce the need for wash-down);
- employing indirect heat-exchange and the use of closed-loop cooling systems;
- re-use or recycling of water within or between process units – within the constraints imposed by their potential to taint products, change odour potential, cause corrosion and increase pollutant concentrations;
- segregating process effluent and rain-water streams both to reduce the hydraulic loading on effluent treatment facilities and to provide the opportunity for partial substitution of mains water input.
- covering bunded areas and locating storage areas inside so that rain-water is not contaminated;
- using dry techniques to abate gaseous and particulate emissions, where appropriate;
- using dry cleaning methods (vacuum, brush) for solids, where practicable;
- substituting wash-water by a solvent wash, where practicable, with the solvent being subsequently re-used.

2.2.2.2 Selection of techniques for effluent treatment

Following an assessment udertaken in accordance with the advice in **Section 2.2.2.1.1**, it is unlikely that any single effluent treatment technique will be adequate to render harmless the waste-water to be discharged. For example:

- A stream containing hexavalent chromium will require reduction to the trivalent form at low pH followed by precipitation at high pH.
- A stream containing cyanide and with a high pH would require cyanide destruction followed by pH adjustment.
- A stream containing organic mercury may need both acidification to convert it to the inorganic form prior to chemical precipitation and a means for rendering harmless the organic compounds.
- Waste waters from the manufacture of precious metal compounds may be displaced by metal scavengers such as copper, zinc or iron, and the metals recovered by filtration before treatment of the bulk of the effluent.

Once all the waste-water issues have been defined, and opportunities for pollution prevention and minimisation identified, consideration will need to be given to the options for treating (abating) the waste water. Treatment can be roughly divided into four groups of techniques which correspond to different stages in treatment. The divisions between the stages are not rigid; some stages will not be necessary and in other situations they may overlap. The technique groupings are:

- **special treatment** of segregated streams, often in-plant, before central treatment or discharge to sewer (**Section 2.2.2.3**);
- **simple pre-treatment** before central treatment or discharge to sewer (**Section 2.2.2.4**);

- **central treatment** at a site effluent treatment plant (Section 2.2.2.5);
- **polishing treatment** before discharge to controlled waters or to sewer (Section 2.2.2.6).

The treatment combination adopted will be process-specific and will reflect both the waste-water characteristics and the nature of the receiving medium (i.e. sewer or surface water). Figure 2.23 and Figure 2.24, respectively, illustrate the potential interactions between the four stages and the potential techniques which may be applied depending on the waste- water characteristics.

Figure 2.23 depicts a hypothetical site consisting of seven PPC activities, some of which are interlinked. This figure is used to show, in particular, the diversity of special treatment techniques that may be applied to individual process streams prior to discharge to central treatment or direct to sewer. It does not cover all potential combinations. Figure 2.24 provides a summary of some of the questions that a process operator could reasonably be expected to address when considering options for waste water treatment.

Figure 2.23: Potential special and pre-treatment waste-water techniques

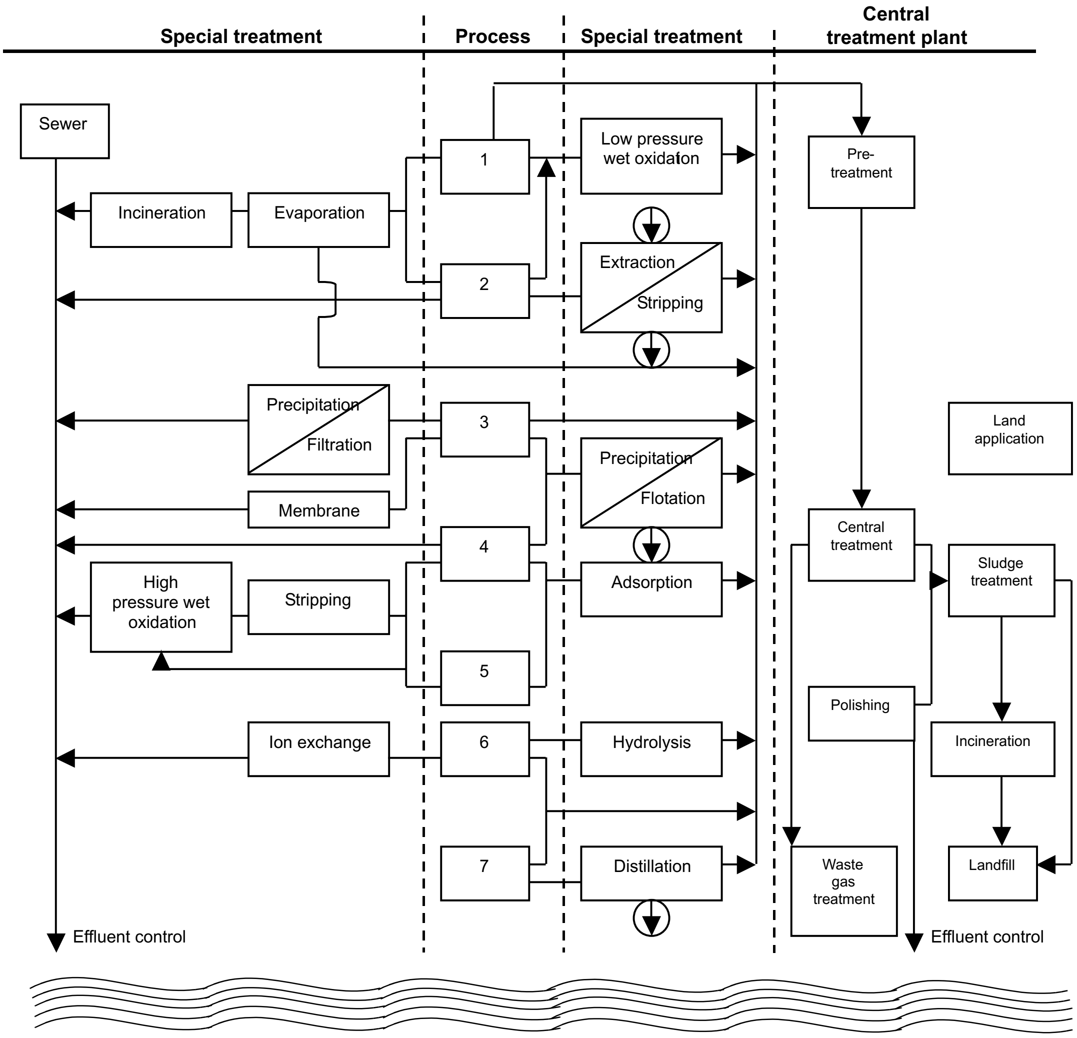
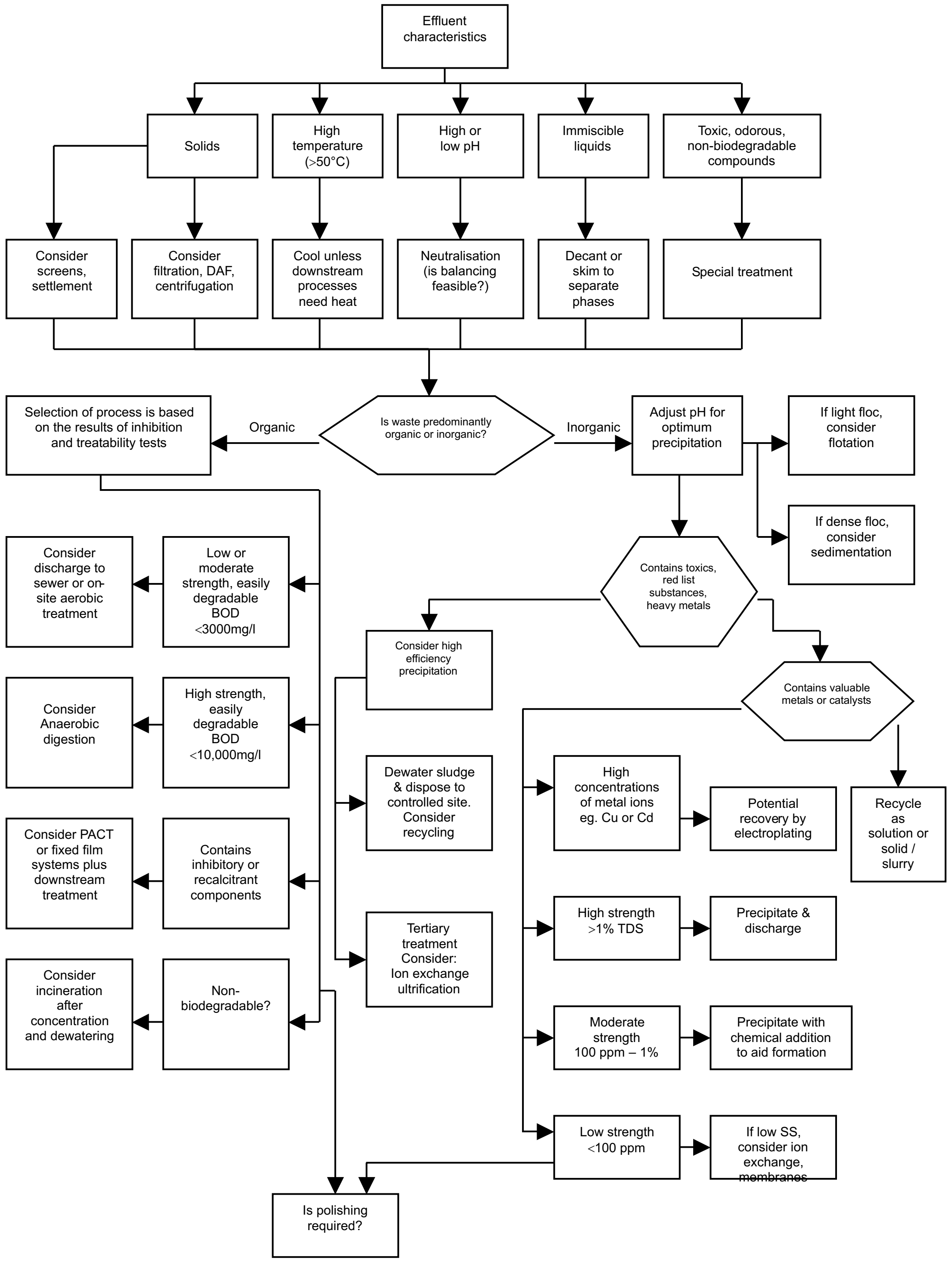


Figure 2.24: Decision tree for selection of waste-water treatment techniques



2.2.2.2.1 Screening of potential techniques

With the large number of effluent treatment techniques potentially available, a preliminary screen of the options may be necessary to identify the few that merit detailed consideration. Screening factors may include, for environmental consideration:

- quality and quantity requirements acceptable to the receiving waters;
- whether the technique(s) can actually abate the constituents of the waste stream;

- downstream sewerage systems and sewerage treatment works, where relevant;
- downstream combined sewer overflows, where relevant;
- containment or storage of waste streams;
- transfer of pollutants to air or to “solid” waste;
- secondary environmental impacts such as noise, odour, visual impairment, etc;

For operational purposes, screening factors may include:

- mechanical and operational reliability;
- space requirements;
- capital and operating costs;
- energy consumption;
- automation and control;

Pilot trials or evaluation studies may need to be performed on the short-listed treatment options to provide data for the final selection. It would be expected that the selection procedure is documented for future reference.

2.2.2.3 Special (or in-plant) effluent treatment

Some waste waters may require special treatment before they can be sent for central treatment because they are particularly toxic, odorous or non-biodegradable or because they are amenable to recovery. Some general examples are:

- For waste streams containing **cyanides or sulphides**, treatment may require a combination of, for example, air or wet oxidation, ion-exchange, air stripping, or activated carbon adsorption.
- For waste streams containing **heavy metals**, treatment may require a combination of, for example oxidation or reduction, precipitation and filtration, ion-exchange, reverse osmosis or electro-chemical techniques.
- For waste streams containing **organics**, treatment may require a combination of, for example, wet oxidation, ion-exchange, reverse osmosis or electro-dialysis.

Solids removal is common in the treatment of discrete effluent streams, but it can occur at any point in a treatment sequence (see **Section 2.2.2.5.2** in the Central treatment section). For example, for removal of heavy metal compounds, it may include screening, filtration, sedimentation, flotation, clarification and evaporation.

Phase-separation and decantation is very common where waste-water streams contain hydrophobic or oily substances which separate into two phases.

Some other techniques for segregated effluents are:

2.2.2.3.1 Vapour stripping techniques

Simple **distillation** may be used to separate organic compounds from waste water, but two common techniques are:

(a) Steam stripping

Steam stripping involves the contacting of steam with the waste water to evaporate volatile compounds. It may be used for VOC or solvent recovery but consideration should be given to collection of all volatiles released and to treatment of the exhaust gas. Steam stripping also removes dissolved carbon dioxide, thereby tending to increase the pH of the effluent stream.

Removal of sulphur contaminants or phosphine can be achieved by steam stripping or air stripping (see next paragraph) - for example, trace amounts of phosphine can be stripped from water or sodium hydroxide scrubbing liquors, and also from by-product phosphoric acid.

(b) Air stripping

Air stripping involves the contacting of the waste water with a current of air or nitrogen. As with steam-stripping, air or nitrogen stripping may be used for VOC or solvent recovery but consideration needs to be given to flammability issues and to the treatment of both the volatiles that may be released and the exhaust air or nitrogen stream.

2.2.2.3.2 Oxidation techniques

Oxidation is usually used as pre-treatment for segregated aqueous streams containing hazardous substances, but it is also used for removing residual traces of contaminants after biological treatment. It can be achieved by the addition of a variety of reagents - ozone (see **Section 2.2.2.6.1** in Polishing techniques), hydrogen peroxide, sodium hypochlorite, pure oxygen, air and UV radiation, and proprietary catalyst systems. An example is the destruction of a wide range of odorous compounds (including ammonia and hydrogen sulphide) by the use of hypochlorite together with a catalyst that enhances the oxidation rate whilst suppressing the formation of chlorine and chlorinated by-products.

Pollutant removal efficiency can be severely affected by the presence of suspended solids or other oxidisable substances. In addition, the pH often has to be controlled to maximise the redox reactions, and some reactions may be so exothermic that cooling is required.

Two specialised oxidation techniques are:

(a) Wet air oxidation

Wet air oxidation involves the oxidation of aqueous wastes (particularly organics-containing) at temperatures in the range of 177 - 315°C and pressures between 7 and 200 bar. The degree of oxidation is dependent upon the temperature, pressure, residence time and nature of the chemical substances present. The oxidation process is autothermal at COD values greater than around 10,000 mg/l (below this concentration auxiliary oxidant may have to be added to the system), and waste waters with greater than 100,000 mg/l COD can be handled if diluted. Waste waters containing high levels of chlorine-containing compounds (or similar potential corrosives) will require the use of corrosion-resistant materials of construction. A variant of the wet air oxidation process works at temperatures lower than 200°C and pressures of 20 bar by utilising an iron-based catalyst and acidification stage at the front end of the process. Wet air oxidation can be particularly suitable for the pre-treatment of non-biodegradable high COD waste waters, prior to conventional biological treatment.

(b) Supercritical water oxidation

Supercritical water oxidation is a high-pressure (>221bar), high-temperature (>374°C) oxidation process that destroys all organic matter dispersed or dissolved in water. Under these supercritical conditions total miscibility occurs and this facilitates the decomposition of organic chemicals. It can be utilised for the removal of organic compounds from wastes containing between 3% and 20% solids, and is particularly suited to the destruction of organic molecules that are not amenable to biological treatment.

2.2.2.4 Pre-treatment prior to central treatment

Many waste waters require pre-treatment (conditioning) prior to the main treatment step (whether on-site or at a sewage treatment works), and in some cases this may be sufficient to preclude the need for further treatment prior to disposal, especially if the effluent is discharged to sewer. The main pre-treatment techniques are:

- **Oil removal** - eg. in a separator, electrostatic coalescer, hydrocyclone, ultrafilter, surface-modified cellulose filter, or by air flotation or by the use of (acceptable) physical coalescing agents.
- **Solids removal** - as noted in the section above, this can occur at several points in a treatment sequence; it is covered in more detail in **Section 2.2.2.5.2**.
- **Control of pH** - is not always easy as the relationship between pH and acid/base concentration is highly non-linear. Multi-stage treatment/dosing is generally better therefore than single stage. See **Section 2.2.2.5.1** below.
- **Equalisation** (balancing) - may address pH and/or temperature problems and it will also reduce peak loads. Balancing tanks may require continuous mixing to prevent settlement, and if the water contains organics or other reducible compounds, there may also be septicity problems.

2.2.2.5 Central waste-water treatment

The type of central treatment required will depend on the characteristics of the waste water - and, depending on the range of process effluents required to be treated, it may include some of the techniques described in the previous sections on Pre-treatment or Special treatment. It may also include some of the Polishing techniques. **Figure 2.24** illustrates the approaches that can be adopted for predominantly inorganic and organic waste waters, respectively. The former are usually treated using chemical coagulation followed by one or more solid/liquid separation steps (e.g. flotation, sedimentation, filtration), the latter using some form of biological technique.

2.2.2.5.1 Control of pH (Neutralisation)

pH adjustment may be required at any of the stages in waste water treatment between in-plant treatment and final discharge to controlled waters or sewer - but, by the end, the effluent should have been dosed with an appropriate acid or alkali to achieve a near-neutral solution. Dosing should be carried out in vessels constructed of suitably resistant material, and of a size and mixing configuration sufficient to achieve a uniform pH.

The control of pH is difficult since the relationship between pH and concentration of reagent is highly non-linear, and most dosing systems are unable to cope with effluents of extreme pH. Where such effluents are likely, intermediate facilities for holding strongly acidic or alkaline effluents should be installed. A typical titration curve demonstrates that multi-stage dosing is better than single stage, and is generally necessary. Control is better still when there is built-in buffering. Automatic control by pH meters should be monitored by regular manual pH measurements and pH meters should be calibrated frequently.

An alternative to conventional lime or sodium hydroxide for the treatment of acidic waste streams (and for treating effluents containing metals) is the use of magnesium hydroxide suspension. It has the advantages in that it is safe and easy to handle, has natural pH buffering properties so tends to reduce the likelihood of pH excursions, and generally reduces the volume of sludge generated. For alkaline effluents, the use of carbon dioxide has some similar advantages.

When dosing effluent with acid, care should always be exercised in case toxic gases are released, e.g. chlorine from hypochlorite, hydrogen sulphide from sulphides, or hydrogen cyanide from cyanides - and where this is a possiblilty, the vents from these vessels should pass to appropriate scrubbing facilities.

As has been noted in **Section 2.2.2.1.1**, the opportunity for the neutralisation of an acid waste stream with an alkaline waste stream should always be considered where compatible streams are available.

2.2.2.5.2 Solids removal

The removal of particulate matter from effluent can be hindered by fluctuations in flow so a flow-balancing facility may be required upstream of any particulate matter removal equipment. On the other hand, removal of finely divided suspended solids (or emulsified oil and grease) can be enhanced by the addition of chemical coagulants/ flocculants.

Techniques for solids removal include coagulation, settlement, flotation, precipitation, dewatering and filtration

(a) Chemical coagulation

Dissolved iron or aluminium salt is added to the waste water and rapidly dispersed and mixed. The pH of the dosed water is adjusted to a level at which the dissolved metal precipitates, usually in the form of a hydrated hydroxide. This pH adjustment is typically achieved by the addition of acid or lime. In some instances a further flocculant aid 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 technique can be used for the removal of suspended solids, metals, some dissolved organic compounds and phosphate, and to reduce the concentration of micro-organisms.

(b) Settlement

If an effluent contains a significant amount of suspended material, the separation of up to 90% of the suspended solids can be achieved by settlement in a clarifier. The clarifier design generally considered to be the most efficient and economical is a circular mechanically-scraped tank - but, depending on the flowrate, a pyramidal-type settlement tank (or multiples in series) may be appropriate.

A suitable treatment or disposal route for the resultant sludge should be identified in advance, and the option of metal recovery should be investigated

Control for settlement processes should include a sludge level indicator and high-level alarm, and, where scrapers are used, loss-of-motion sensors should be used.

Sludge that includes biodegradable organics containing sulphur will have a tendency to produce hydrogen sulphide unless properly aerated.

(c) Flotation

An alternative to sedimentation is flotation - either induced or dissolved-air flotation (DAF) - though it is less common in the chemical industry. The required tank size is substantially smaller but more ancillary equipment is needed, so the overall capital cost is higher for sites with large effluent volumes (more than 200 m3/ day).

In DAF units a controlled release of pressure produces a rising blanket of micro-bubbles as the dissolved air degasses. The bubbles carry suspended solids to the surface of the tank where they are removed by surface skimmers. Either circular or rectangular tanks can be employed and retention times are typically designed to be 20-40 minutes at peak hydraulic loading (influent plus recycle). The addition and mixing of flocculants and pH control chemicals can be made, as necessary, prior to raw effluent entering the tank.

Where volatile chemicals may be present, an assessment of the impact of the release to air of any of those chemicals due to the action of aeration must be undertaken.

Control of the units should include continuous monitoring of the air supply and of continuous operation of the skimmers on the surface.

(d) Precipitation

Chemical precipitation of dissolved heavy metals is the most common treatment method for metal ions encountered, and may be accomplished either in batch or continuously. Generally, the precipitate is the metal hydroxide, sulphide or carbonate. The pH is set at the optimum for maximum precipitation so the final effluent may require subsequent pH adjustment before release to water.

Precipitates are separated by settling or by filtration, or a combination of both - and pressure filters, media filters or vacuum filters may be used (see sub-sections (b) and (e), respectively). In practice, in order to achieve a satisfactory level of metal removal in many cases, enhancing techniques such as secondary precipitate generation or filter aid addition may also be necessary.

Where practicable, the precipitated sludge should be dewatered to obtain a sludge that is suitable for metal recovery; (see sub-section (f) below).

Alkaline precipitation relies on the low solubility of most heavy-metal hydroxides in water. However, they usually precipitate as very small or colloidal particles so, to obtain a heavier precipitate and more efficient separation, polyelectrolyte coagulating agents are often added.

The most common alkali precipitants are calcium hydroxide slurry and sodium hydroxide solution, and the appropriate choice should be made taking account of all relevant factors including the potential for recovery of the metal from the precipitate. In some cases, magnesium hydroxide suspension may offer a number of advantages, including reduced sludge volume and a natural buffer pH of 9.5, which can give better cost/ material effectiveness.

Hydroxide solubilities differ markedly with pH and species so it is important to establish the optimum pH control point for each particular waste stream. This can be difficult when a number of different metal ions are present as individual optima vary, for example, from pH 4.3 for ferric hydroxide to pH 9.3 for nickel (II) hydroxide - and a programme of test work may have to be undertaken to demonstrate effective metal removal. Multi-stage precipitation may be necessary, and other factors such as residence time, particle growth and choice of coagulant, if any, will also need to be investigated and justified as BAT in the Application for a Permit.

Sulphide precipitation may give higher removal efficiency but it requires a high degree of control to avoid excess sulphide in the final effluent, and hydrogen sulphide generation from sludge. It may be appropriate to use both hydroxide and sulphide in a multi-stage system at increasing pH, and with a final long-residence time sulphide stage.

Carbonate precipitation by the use of sodium carbonate or carbon dioxide may be an appropriate method in some cases, e.g. streams containing nickel, lead or cadmium compounds.

Hydroxide and carbonate precipitation may not be sufficient to remove metal cations in one stage, so further precipitation stages or a different tertiary treatment - such as ion exchange for full cation removal - may be necessary. Precipitation reactions can be affected by the presence of complexing agents or other cations and anions, and there are specific reagents available for enhancing the precipitation efficiency of particular ions.

Co-precipitation is a technique often used for heavy-metals removal. Ferric hydroxide naturally coagulates in water so its precipitation results in very effective agglomeration of colloidal material, with co-precipitated heavy metals naturally adsorbing to the surface of the iron solids. Ferric hydroxide precipitates tend to be denser than other metal hydroxide precipitates and hence are easier to settle and remove.

(e) Filtration

Precipitated wastes as well as intermediate or product materials are often isolated as solids. The maximum retention of solids on the filter is generally the aim and, in the case of batch production, this usually involves recycling the filtrate until the solids content is effectively irreducible. As with 2-phase liquid separations, in liquid-solid separations the product (the filter cake) is usually washed, often with a discrete number of rinses - and wherever possible, the rinse water from the last wash of one batch should be used for the first wash of the next batch. In some cases it may be possible to re-use even earlier stage rinse-waters than the last one.

Methods for discharging the solid filter cake vary with the type of filter but the method selected should demonstrably minimise loss or spillage of solids to the water environment. Where the filter requires cleaning, losses of solids to the water environment should be defined and justified as the minimum achievable - and, where practicable, clean-down water should be re-used. The replacement of filter medium can also generate a significant clean-down stream but, sometimes, filter medium replacement can be minimised on multi-product chemical installations plant by dedicating filter cloths or elements for specific products and saving them for re-use.

Since the integrity of the filter medium is crucial to the operation, a means of preventing its failure and consequent releases to effluent streams is required - and this often takes the form of a guard filter, or a collection vessel, or an automatic detection and shut-down system.

(f) De-watering of sludges and filter cake

Dewatering of sludge wastes is a common method of waste volume reduction, and mechanical dewatering in addition to, or instead of, gravity thickening is appropriate for many effluent streams associated with the manufacture and use of metal compounds. The product is a dewatered solid, which may be handled easily and with less risk of spillage than a slurry.

A variety of dewatering facilities are available - including centrifuges, filter-belt presses, filter-plate presses and rotary vacuum filters - but polyelectrolyte addition (at 1-5 kg per tonne dry solid) is often necessary as a dewatering aid. The choice of technique is generally dependent on cost, space availability and the degree of dewatering required - though filter-plate presses are frequently appropriate.

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

2.2.2.5.3 Biological treatment

Whilst this option is usually considered where the waste water has a significant organic content, is biodegradable and is present in large volumes, it does have some applications in the Inorganics sector. There are many technique variants and common types include trickle beds (biological filtration), rotating biological contactors, fluidised-bed systems, activated sludge, deep shaft and polishing filters.

All biological effluent treatment plant needs to be acclimatised to the effluent feed and nutrient conditions so under most circumstances flow-balancing arrangements or buffer tanks are required to control flows and pollutant loads to the plant, and to allow checks on compatibility prior to treatment. The pH of the feed should be kept between 6.5 and 8.5 to maintain optimum biological activity. Consideration should also be given to the consequences of loss of activity due to the introduction of toxic compounds, including having procedures to prevent such an event and maintaining a sock of seed inoculum.

For this sector, biological treatment of effluent containing cyanide is possible but is generally susceptible to shock loads and requires long residence times. Similarly, effluent containing sulphur compounds is possible but also susceptible to shock load - and strict control conditions are required to prevent formation and release of hydrogen sulphide or mercaptans and consequent problems with odour beyond the installation boundary.

Naturally occurring sulphate-reducing bacteria can be used to generate hydrogen sulphide which in turn can be used to precipitate out sulphides in waste waters containing metal salts.

Four groupings of biological techniques are discussed further below:

(a) Aerobic techniques

There are many aerobic techniques and they have been used extensively in chemicals sectors, particularly the activated sludge technique. It is generally the most cost-effective, safe and reliable method of removing biodegradable organics in waste waters.

Control of pH to approximately neutral, equalisation and suspended solids removal if their concentration is too high, should precede the activated sludge system. Activated sludge treatment involves an aeration step followed by solid–liquid separation, with recycle of a portion of the solids (activated sludge). The basic system consists of 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 traditional activated sludge plant requires a relatively large area. In some industrial applications this may limit its application. Some variants have been designed to overcome this problem, e.g. the deep tank system, aerated filters and the use of oxygen

A number of issues need to be considered when applying aerobic techniques. These include:

- V*olatile emissions* - volatilised organics may contribute to cross-media contamination, odours may arise and health risks be posed to plant operators.
- *Inhibition.* Some chemicals can inhibit the growth or respiration of the biomass that forms the basis for aerobic techniques, reducing the efficiency of treatment. The possibility or extent of inhibition for any given waste water is usually only predictable using inhibition tests - for which standard assessment methods are available.
- *Acclimatisation.* The biomass is a living and often changing entity. Slow increases in the concentration of a contaminant in the waste water may allow the biomass to adapt but shock concentrations may not be treated effectively and may even threaten the biological system.
- *Solids.* The residual sludge may be contaminated with metals, pathogens and toxic chemicals. This gives potential for cross-media contamination and the sludge may require special disposal.
- *Recalcitrant organics.* These are organic chemicals that are resistant to biological treatment and which may have an adverse impact on the receiving waters.
- *Odour.* Volatilisation of chemicals, digestion by-products, septicity of sludges and poor sludge management procedures can generate odour.
- *Nutrients.* The biomass needs a suitable level of nutrients (carbon, nitrogen, oxygen, phosphorus, sulphur, etc) to survive. If the waste water does not contain the correct balance, dosing of nutrients to the treatment plant may be required

(b) Constructed wetlands

Constructed wetlands (reed beds) may be used in situations where space is available to build them and the waste water contains predominantly organic or biodegradable wastes of a relatively low strength <2000 mg/l (BOD_5).

They have the advantages of low operating and capital costs, being easy to operate and facilitating regeneration of natural habitats. However, VOCs may be lost to the atmosphere from the surface of the reed bed, and solids or non-biodegradable substances may accumulate in the bed, reducing removal efficiency - though in some cases the capture of toxic species such as heavy metals and their accumulation in the biomass is an advantage.

(c) Anaerobic techniques

Anaerobic digestion is a biological treatment technique for the degradation of organics in an oxygen-free environment. The microbiology is complex and conditions such as pH and loading must be closely controlled. The technique is preferred for very strong organic streams but certain organic compounds may have an inhibitory effect on the process and some are only poorly removed. Anaerobic treatment is only likely to be used in this sector for specialist purposes.

(d) Enhanced biological treatment

A number of techniques have been developed to enhance aerobic and anaerobic biological treatment, particularly for those substances which are difficult to remove in the standard treatment process. These include:

- Fixed film processes which use a solid medium to support the micro-organisms. The use of this medium may make the process more tolerant to fluctuations in load because of the large biomass available.
- Bio-augmentation which uses supplementary bacteria or immobilised enzymes to deal with specific compounds that are resistant to normal biological treatment.
- Biological treatment with adsorption which uses a suspended growth system supplemented by dosing of powdered activated carbon (PAC). The PAC adsorbs toxic chemicals to protect the biological system, thereby increasing its robustness, stability and performance, and similarly protects the receiving waters by removing those toxic substances.

These techniques can often be applied to upgrade the performance of central, biological treatment at relatively low cost.

2.2.2.6 Polishing techniques

Polishing may be required as the final treatment stage before discharge to sewer or to controlled waters to remove substances that, whilst not having an adverse effect on subsequent treatment stages (i.e. sewage treatment works), may have an unacceptable impact on the receiving water. Some polishing techniques may occasionally be applied as special treatment upstream of central treatment, but this is relatively rare as polishing techniques are relatively costly and there is always the potential for competition between general pollutants and the polishing technique's target pollutants. If central treatment is applied first the bulk of the load in the waste water is removed before the polishing stage.

2.2.2.6.1 Ozone-based systems

Ozone-based systems are particularly useful for dealing with recalcitrant COD. Ozone (O_3) is usually generated by discharging a high-voltage electrical current through dry air or pure oxygen. Dry air must be used or else nitric acid is formed. Efficient cooling of the ozone production elements is required. Recent developments in ozone generation use medium-frequency rather than high-frequency electric currents, and oxygen rather than air. This reduces energy consumption and increases the ozone concentration, thus improving removal efficiencies substantially. The ozone is added to the waste water in specially designed contact tanks. A number of variations exist, including:

- **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 for disinfection.
- **Ozone with ultraviolet irradiation** uses reactors fitted with UV lights and operating under pressure to keep the ozone in solution. The use of combined UV/ozone systems allows a wider range of organic substrates to be treated in a shorter reaction time. The use of this technique may be limited by turbidity, which results in poor transmission of UV through waste water and hence limits removal efficiencies.
- **Ozone with ultraviolet irradiation and hydrogen peroxide** uses hydrogen peroxide to enhance oxidation by generating more 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 may be especially useful for the removal of aromatic halides, which readily adsorb UV. On the other hand, the technique is not best applied to poorly-nitrified or high ammonia-containing effluents because ammonia competes with the target organics for the hydroxyl radicals.
- **Ozone with adsorption pre-concentration** is 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 a metal hydroxide, which adsorbs the target substance(s). This forms a slurry, which is then mixed with ozone and the target substances destroyed. The ozonation is catalysed by the metal hydroxide.

The capital and operating costs of ozone treatment are high. The high capital cost is mainly due to the cost of ozone generation equipment, and the high operating costs are mainly due to electricity usage. Each of the variants on the basic ozone system will increase overall costs.

2.2.2.6.2 Adsorption by activated carbon or zeolites

Activated carbon adsorption is available in two forms:

- **Granular activated carbon (GAC)** is usually used in fixed-bed reactors with the waste water being passed through it downwards. It can be used for the removal of low concentrations of metal species, and to polish a final effluent to provide recyclable water. The beds have to be removed periodically for specialist off-site regeneration and then, before re-use, the GAC has to be acid-washed to avoid reduced capacity after regeneration. Problems can arise if other substances that preferentially adsorb to the bed are present - and this can lead to the bed being exhausted rapidly - but TOC (total organic carbon) can often be reduced by up to 99%.
- **Powdered activated carbon (PAC)** is superior to GAC in terms of its specific capacity for adsorbing organics and the consistent quality of the cleaned water, but it usually offers fewer opportunities for recycling and its capacity depends on the other organics present. The removal of PAC from the waste water requires a sedimentation stage and PAC is therefore usually applied before the main treatment stage (see enhanced biological treatment in **Section 2.2.2.5.3**, sub-section (d).)

PAC can be added to activated sludge processes to enhance performance. Typical dosage levels are of the order of 20-200 mg/l of effluent feedstock. Its usage results in lower variability of effluent quality and the removal of non-biodegradable organics.

When there is a small or intermittent application of PAC, the carbon is disposed of with the excess sludge. Continuous application at larger plants, however, requires regeneration of the carbon - and this can be accomplished by the use of wet air oxidation. PAC usage in biological treatment systems can help to reduce or eliminate in some case, the problem of nitrification caused by the presence of toxic organics.

Zeolites can be used to adsorb ammonia or toxic metals such as cadmium from waste waters.

2.2.2.6.3 Ion exchange resins and macroreticular resins

Ion exchange units consist of resin beds designed to remove undesirable cations or anions from waste water streams. The water flows through the ion exchange beds and the target ions bind to the resin material, displacing comparatively innocuous ions - hydrogen or sodium ions for cations, and hydroxyl ions for anions. Ion exchange resins consist of an organic or inorganic network structure with attached ionisable functional groups.

Treatment of waste water by ion exchange involves a sequence of operating steps. The waste water is passed through the resin until breakthrough starts to occur; the bed is then regenerated by backwashing with water followed by regenerant (mineral acid, alkali or salt) prior to re-use. Regeneration produces a fixed volume of effluent per ion-exchange exhaustion cycle, and disposal of this small volume of liquor (which now contains the displaced polluting ions) is an important factor in minimising environmental harm; systems have been developed specifically to minimise environmental impact.

The advantages of ion exchange are that energy consumption is relatively low and the technique works well on dilute waste streams. The main disadvantages are the relatively high cost of chemicals for regeneration and, because it is a batch process, two or more parallel streams are required for continuous operation.

Ion exchange systems can remove **cyanide** and **sulphide** from effluents but, they do not destroy cyanide so subsequent treatment of cyanide-containing regeneration solutions would be required

Macroreticular resins are similar in concept but are non-polar systems which have been developed for the removal of specific non-polar organic compounds, typically with success rates in the range 85 - 99%.

Removal of fine particlulates prior to exchange in resin systems is usually necessary, because fouling can lead to deteriorating performance.

2.2.2.6.4 Membrane processes

Membrane processes concentrate solutions by selective filtration and usually produce a purified filtrate stream and a concentrated stream. Membrane techniques include: ultrafiltration, reverse osmosis, membrane filtration and pervaporation. The efficiency of the filtration processes depends upon the difference in size between the pore and the particle to be removed or retained, whilst in reverse osmosis, the efficiency depends on how well the membrane rejects the flow of solute whilst allowing the flow of solvent.

Polymeric membrane technology has developed to extend membrane life and overcome fouling problems - there are direct cleaning membrane units - but most membrane processes tend to be developed for specific effluents. They can be used both to clean up waste water for re-use and to recover material for recycling, but the choice of technique should be justified as being as good as, and preferably better than, other available techniques.

Common membrane techniques are described in sub-sections (a) to (d) below. Newer techniques include the use of gas-filled membranes (hydrophobic microporous membranes in which the pores are filled with gas) which, when inserted between an aqueous solution containing a volatile component and an absorbent solution such as sodium hydroxide or hydrochloric acid, allow the volatile component to diffuse preferentially through the membrane and be absorbed by the stripping solution.

(a) Pervaporation

Pervaporation is a process that uses membranes for the removal of organic compounds from water. It is a technically feasible and economically attractive method for the treatment of waste water containing VOCs and chlorinated solvents, and compares favourably with steam stripping and carbon adsorption. The component to be separated is ‘evaporated’ from the effluent through a membrane under vacuum, and then recovered by condensation - so pervaporation is particularly suited to waste waters containing relatively hydrophobic but volatile organics such as chlorinated solvents, naphthas, toluene and benzene.

A wide variety of organic polymers is available for the removal of specific target contaminants, and it has been successfully adopted in the following applications:

- pollution control of dilute solutions of hydrophobic solvents (e.g. 1000 ppm benzene in water);
- solvent recovery from process waste waters;
- volume reduction of mixed solvent hazardous waste.

(b) Ultrafiltration and reverse osmosis

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

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

Membranes can be classified according to their molecular weight cut-off point (MWCO), ie the approximate molecular weight above which molecules cannot pass through the membrane. **Table 2.6** shows situations in which such techniques can be applied

Fouling of the membrane can occur. This can be reduced primarily by designing the plant to maintain high velocities and turbulence at the membrane surface, but may sometimes require the dosing of anti-scaling compounds to the waste water or physical cleaning. Some compounds may adsorb to the membrane, reducing its effectiveness, whilst others, particularly those containing chlorine, may damage it. Membranes produce a highly concentrated waste stream that requires incineration or other specialist disposal technique.

Table 2.6: Technique application ranges for a number of different types of membrane

	Pore size (micrometres)	Molecular weight cut-off (MWCO)	Application
Microfiltration	0.1 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

(c) Ceramic membranes

Ceramic membranes consist of a rigid structure, produced from sintered alumina or zirconia. The waste water is fed down the centre of the sintered tubes and the filtrate collected on the outside. Compared to polymer membranes, ceramic-based systems can be heated, back-washed and cleaned using solvents. Furthermore they exhibit a much greater resistance to chemicals and are much less susceptible to blocking by suspended solids.

The major disadvantages are that ceramic membranes 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, thus vibration may cause problems.

2.2.2.7 Electrochemical techniques

Metals can be extracted from aqueous streams by sacrificial exchange, for example, adding zinc or iron filings to an aqueous solution of lead salts results in the precipitation of lead, zinc and iron being more electropositive than lead. Another example is the treatment of platinum and palladium effluents with iron.

This displacement process does result in the release of another metal into the effluent stream so consideration should be given to the consequences and the possible need for further treatment of the effluent stream.

Electrochemical-deposition - Metal cations may be electroplated on to cathode materials in electrochemical cells and provide the potential for the plated metal to be re-used. Cation removal efficiency is very dependent on specific physical and chemical factors and electrochemical-deposition alone may not always achieve total cation removal. Electrochemical cells are typically used for bulk removal from high-concentration solutions such as rinse-waters in plating activities or spent ion-exchange liquors, but there are electrochemical cells available for efficient recovery at much lower metal concentrations in effluent streams.

2.2.2.8 Summary of effluent treatment techniques

Table 2.7 summarises the types of technique that are available to deal with specific chemical compounds or families.

In this sector it is more common for processes to be upgraded rather than new ones constructed. The main issue is therefore the identification of techniques that can improve the performance of existing waste-water treatment stages. The use of PAC and bioaugmentation, in particular, offer opportunities for enhanced performance at relatively low cost.

Table 2.7: Waste-water abatement techniques

Contaminant	Abatement techniques
Suspended solids	Coagulation/flocculation Sedimentation Flotation Filtration
pH	Neutralisation
Insoluble organics	Separators
Biodegradable organics	Aerobic Anaerobic
Volatile organics	Air stripping Steam stripping Distillation Activated carbon Evaporation

Table 2.7: Waste-water abatement techniques

Contaminant	Abatement techniques
Metals	Chemical coagulation Ion exchange Electrochemical recovery
Ammonia	Ammonia stripping Oxidation
Nutrients (N)	Suspended-growth nitrification and denitrification variations Fixed-film nitrification and denitrification variations Ion exchange Breakpoint chlorination Natural systems
Nutrients (P)	Metal-salt addition Lime coagulation Biological phosphorus removal Biological–chemical phosphorus removal
Nutrients (N+P)	Biological removal
Refractory organics	Carbon adsorption Ozonation Supercritical water oxidation Wet air/oxygen oxidation Chemical oxidation
Dissolved organic solids	Ion exchange Membranes Carbon adsorption

2.2.3 Point source emissions to groundwater

Groundwater protection legislation

The Groundwater Regulations for the UK came into force on 1 April 1999, and an IPPC Permit will be subject to the following requirements under these Regulations.

i. The Permit shall not be granted at all if it would allow the *direct discharge* of a List I substance (Regulation 4(1)) - except in very limited circumstances (see Notes 1 and 2, below).

ii. If the Permit allows the disposal of a List I substance or any activity that might lead to an *indirect discharge* of a List I substance then *prior investigation* (as defined in Regulation 7) is required and the Permit shall not be granted if this reveals that indirect discharges of List I substances would occur. In any event, conditions to secure the prevention of such discharges must be imposed (Regulation 4(2) and (3)).

iii. In the case of List II substances, Permits allowing direct discharges or possible indirect discharges, cannot be granted unless there has been a prior investigation and conditions must be imposed to prevent groundwater pollution (Regulation 5).

iv. The Regulations contain further detailed provisions covering *surveillance* of groundwater (Regulation 8); conditions required when direct discharges are permitted (Regulation 9); when indirect discharges are permitted (Regulation 10); and review periods and compliance (Regulation 11).

The principles, powers and responsibilities for groundwater protection in England and Wales, together with the Environment Agency’s policies on this, are outlined in the Environment Agency’s document **Releases to water references**. This outlines the concepts of vulnerability and risk and the likely acceptability from the Regulator’s viewpoint of certain activities within groundwater protection zones. These are categorised as:

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

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

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

Note 1 The Regulations state that, subject to certain conditions, the discharges of List I substances to groundwater may be authorised if the groundwater is “permanently unsuitable for other uses”. Advice must be sought from the Regulator where this is being considered as a justification for such discharges.

Note 2 List I and List II refer to the list in the Groundwater Regulations and should not be confused with the similar lists in the Dangerous Substances Directive (see **Appendix 4**)

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

1 In general, there should be no permitted releases to groundwater of either a direct or indirect nature.

2 If there are releases to groundwater and they are to continue, the requirements of the Regulations, as summarised above, must be complied with.

2.2.4 Control of fugitive emissions to air

Dust emissions and VOC emissions are the most common fugitive emissions across the Inorganics sector as a whole though fugitive releases of substances peculiar to the installation itself are often the most significant fugitive emissions. Fugitive emissions of these substances are referred to in the appropriate process descriptions in **Section 2.1**, together with some techniques required to prevent them.

Where VOCs are a significant proportion of fugitive losses, the corresponding part (i.e. Section 2.2.4) of the Large Volume Organic Chemicals guidance, S4.01 (**Ref 23**), should be consulted for specific methods of monitoring and minimisation.

As part of the Application for a Permit the Operator should identify all the sources and causes of significant fugitive emissions to air from the installation, estimating the magnitude for each substance - and indicating what techniques might be deployed to reduce them.

Indicative BAT requirements for fugitive emissions of VOCs and particulates to air

1 **Dust** - The following general techniques should be employed where appropriate:

- Covering of skips and vessels
- Avoidance of outdoor or uncovered stockpiles (where possible)
- Where dust creation is unavoidable, use of sprays, binders, stockpile management techniques, windbreaks and so on
- Regular wheel and road cleaning (avoiding transfer of pollution to water and wind blow)
- Closed conveyors, pneumatic or screw conveying (noting the higher energy needs), minimising drops. Filters on the conveyors to clean the transport air prior to release
- Regular housekeeping
- Enclosed silos (for storage of bulk powder materials) vented to fabric filters. The recycling of collected material should be considered under Section 2.6.
- Enclosed containers or sealed bags used for smaller quantities of fine materials

2 **VOCs**

- When transferring volatile liquids, the following techniques should be employed – subsurface filling via (anti-syphon) filling pipes extended to the bottom of the container, the use of vapour balance lines that transfer the vapour from the container being filled to the one being emptied, or an enclosed system with extraction to suitable abatement plant.
- Vent systems should be chosen to minimise breathing emissions (for example pressure/ vacuum valves) and, where relevant, should be fitted with knock-out pots and appropriate abatement equipment.
- Maintenance of bulk storage temperatures as low as practicable, taking into account changes due to solar heating etc.
- The following techniques should be used (together or in any combination) to reduce losses from storage tanks at atmospheric pressure:
  - Tank paint with low solar absorbency
  - Temperature control
  - Tank insulation
  - Inventory management
  - Floating roof tanks
  - Bladder roof tanks
  - Pressure/vacuum valves, where tanks are designed to withstand pressure fluctuations
  - Specific release treatment (such as adsorption condensation)

3 For Information on Odour, see **Section 2.2.6**.

2.2.5 Fugitive emissions to surface water, sewer and groundwater

Fugitive emissions - primarily from leaks and spillages - may occur into cooling water, site drainage water and groundwater. Their control must form part of a programme of good design, monitoring, maintenance and operating procedures. Aspects of these controls will be found in several parts of this Note, but they are brought together and summarised in this section.

Cooling Water

Leaks of process fluids into cooling water in heat exchangers are a frequent source of contamination. Monitoring of the cooling water at relevant points should be appropriate to the nature of the process fluids. In a recirculatory cooling system, leaks can be identified before significant emission to the environment has occurred. The potential for environmental impact is likely to be greater from a once through system. Planned maintenance can help to avoid such occurrences.

Site Drainage Water

Storage tanks and process vessels should be bunded. The bunding arrangements should be subject to risk assessment and be capable of containing at least 110% of the capacity of the largest tank within any one bund. Bunds should be impermeable and should have no direct connection to drains. The roofing of bunded areas can minimise the volume of potentially contaminated storm water. Bunds not frequently visited should be fitted with a high-level probe and an alarm as appropriate. Bunds should be regularly inspected for structural integrity by a competent person. The Environment Agency has issued guidance on tank storage.

In addition to sealed bunds, possible measures to reduce contamination from large storage tanks include:

- Double-walled tanks, and
- Leak detection channels.

Hard surfacing should be provided in areas where accidental spillage or leakage may occur, e.g. beneath prime movers, pumps, in storage areas, and in handling, loading and unloading areas. The surfacing should be impermeable to process liquors.

Hard surfacing of areas subject to potential contamination should be drained such that potentially contaminated surface run-off is not allowed to discharge to ground.

Stocks of suitable absorbents should be held at appropriate locations for use in mopping up minor leaks and spills, and should be disposed of to leak-proof containers.

Particular care should be taken in areas of inherent sensitivity to groundwater pollution. Poorly maintained drainage systems are in many cases known to be the main cause of groundwater contamination and surface/above-ground drains are preferred to facilitate leak detection (and to reduce explosion risks).

Additional measures could be justified in locations of particular environmental sensitivity. Decisions on the measures to be taken should take account of the risk to groundwater, taking into consideration the factors outlined in the Agency document, Policy and Practice for the Protection of Groundwater, including groundwater vulnerability and the presence of groundwater protection zones.

Groundwater Vulnerability

The vulnerability of groundwater to contaminants will depend on the natural characteristics of any given site, specifically on the physical, chemical and biological properties of soil and rocks beneath the site. The Environment Agency has produced a series of maps of England and Wales, which provide a guide to potential groundwater vulnerability. Source Protection Zones are intended to aid protection by defining annular zones around each major potable source, including springs, boreholes and wells, based on travel times.

Surveys of plant that may continue to contribute to leakage should also be considered, as part of an overall environmental management system. In particular, operators should consider undertaking leakage tests and/or integrity surveys to confirm the containment of underground drains and tanks.

As part of the Application, the Operator should identify and, where possible, quantify significant fugitive emissions to water, sewer or ground from all relevant sources, and estimate the proportion of total emissions that are attributable to fugitive releases for each of the main substances releases.

Some common examples of sources of fugitive releases to waters and their preventive measures are given in the BAT box below.

Indicative BAT requirements for fugitive emissions to water (Sheet 1 of 2)

1 For **subsurface structures**:
- establish and record the routing of all installation drains and subsurface pipework;
- identify all sub-surface sumps and storage vessels;
- engineer systems to minimise leakages from pipes and ensure swift detection if they do occur, particularly where hazardous (ie. Groundwater-listed) substances are involved;
- provide secondary containment and/or leakage detection for sub-surface pipework, sumps and storage vessels;
- establish an inspection and maintenance programme for all subsurface structures, eg. pressure tests, leak tests, material thickness checks or CCTV

2 All sumps should:
- be impermeable and resistant to stored materials;
- be subject to regular visual inspection and any contents pumped out or otherwise removed after checking for contamination;
- where not frequently inspected, be fitted with a high level probe and alarm, as appropriate;
- be subject to programmed engineering inspection (normally visual, but extending to water testing where structural integrity is in doubt).

3 For **surfacing**:
- design appropriate surfacing and containment or drainage facilities for all operational areas, taking into consideration collection capacities, surface thicknesses, strength/reinforcement; falls, materials of construction, permeability, resistance to chemical attack, and inspection and maintenance procedures;
- have an inspection and maintenance programme for impervious surfaces and containment facilities;
- unless the risk is negligible, have improvement plans in place where operational areas have not been equipped with:
  - an impervious surface

Indicative BAT requirements for fugitive emissions to water (Sheet 2 of 2)

- spill containment kerbs
- sealed construction joints
- connection to a sealed drainage system

4 All **above-ground tanks** containing liquids whose spillage could be harmful to the environment should be bunded. For further information on bund sizing and design, see the **Releases to water references**. Bunds should:

- be impermeable and resistant to the stored materials;
- have no outlet (that is, no drains or taps) and drain to a blind collection point;
- have pipework routed within bunded areas with no penetration of contained surfaces;
- be designed to catch leaks from tanks or fittings;
- have a capacity greater than 110 percent of the largest tank or 25 percent of the total tankage, whichever is the larger;
- be subject to regular visual inspection and any contents pumped out or otherwise removed under manual control after checking for contamination;
- where not frequently inspected, be fitted with a high-level probe and an alarm, as appropriate;
- where possible, have tanker connection points within the bund, otherwise provide adequate containment;
- be subject to programmed engineering inspection (normally visual, but extending to water testing where structural integrity is in doubt).

5 **Storage areas for IBCs, drums, bags, etc,** should be designed and operated to minimise the risk of releases to the environment. In particular:

- Storage areas should be located away from watercourses and sensitive boundaries, (eg. those with public access) and should be protected against vandalism.
- Storage areas should have appropriate signs and notices and be clearly marked-out, and all containers and packages should be clearly labelled.
- Where spillage of any stored substance could be harmful to the environment, the area should be appropriately kerbed or bunded.
- The maximum storage capacity of storage areas should be stated and not exceeded, and the maximum storage period for containers should be specified and adhered to.
- Appropriate storage facilities should be provided for substances with special requirements (eg. flammable, sensitive to heat or light) and formal arrangements should be in hand to keep separate packages containing incompatible substances (both “pure” and waste).
- Containers should be stored with lids, caps and valves secured and in place - and this also applies to emptied containers.
- All stocks of containers, drums and small packages should be regularly inspected (at least weekly).
- Procedures should be in place to deal with damaged or leaking containers.

2.2.6 Odour

Many of the substances used in the processes in the Inorganics sector have some potential to cause odour, but the odour threshold of the substances differs widely. Some compounds, such as hydrogen sulphide and mercaptans or ammonia and amines, are particularly pungent but many other compounds such as chlorine or sulphur dioxide can also cause offence at low levels.

The generic techniques for preventing or minimising process and fugitive emissions to air included in **Section 2.2.1** and **Section 2.2.4**. are the basis for odour prevention from the process, and where there are highly odorous materials, it is necessary to use the strictest techniques to prevent trace emissions. These are included as special techniques in the descriptions of the relevant processes in **Section 2.2**.

Odorous compounds can be emitted from the treatment of otherwise innocuous substances, for example in the biological treatment of waste water. Incorrectly designed or operated facilities intended to be aerobic may not provide sufficient aeration and may allow the formation of odorous compounds in anaerobic conditions. Volatile compounds may be released on first exposure of the waste water to the atmosphere. Their emission may need to be prevented by covering the tank or separator and recovering the compounds.

In an Application for a Permit, the Operator should supply a level of detail in keeping with the risk of causing odour-related annoyance at sensitive receptors. Where an installation poses no risk of odour-related environmental impact because the activities are inherently non-odorous, a simple justification should normally suffice.

However, where odour could be a problem, the Operator should assess the situation carefully and supply the information as indicated below to demonstrate that BAT is being used:

- Information relating to sensitive receptors, in particular the type of receptor, location relative to the odour sources and an assessment of the impact of odorous emissions on those receptors. (This should normally be available before a Permit is issued, but where very detailed information has to be obtained the Operator may be able to secure an agreement to supply it as part of an Improvement Programme.)
- An overview of any complaints received, what they relate to (source/operation) and remedial action taken.
- The types and source of odorous substances used or generated, intentional and fugitive (unintentional) release points and monitoring undertaken.
- Actions taken to prevent or minimise
  - – A description of the actions taken to prevent and/or minimise odour annoyance for each odour source.
  - – A demonstration that the indicative BAT requirements are being complied with.
  - – Identification of any circumstances or conditions which might compromise the ability to prevent or minimise odour annoyance, and a description of the actions that will be taken to minimise the impact.

There may be a requirement placed upon the Operator to provide some or all of this information in the form of an odour management statement. See the **Odour management statement** for a typical log book.

The use of appropriate sections of H4 Horizontal Guidance for Odour - Part 1 (Regulation and Permitting) and Part 2 (Assessment and Control) is advised.

Indicative BAT requirements for odour control (Sheet 1 of 2)	
1	The requirements for odour control will be installation-specific and depend on the sources and nature of the potential odour. In general:
2	Where odour can be contained, for example within buildings, the Operator should maintain the containment and manage the operations to prevent its release at all times.

Indicative BAT requirements for odour control (Sheet 2 of 2)

3 Where odour releases are expected to be acknowledged in the Permit, (i.e. contained and treated prior to discharge or discharged for atmospheric dispersion):

- For existing installations, the releases should be modelled to demonstrate the odour impact at sensitive receptors. The target should be to minimise the frequency of exposure to ground level concentrations that are likely to cause annoyance.
- For new installations, or for significant changes, the releases should be modelled and it is expected that the Operator will achieve the highest level of protection that is achievable with BAT from the outset.
- Where there is no history of odour problems then modelling may not be required although it should be remembered that there can still be an underlying level of annoyance without complaints being made.
- Where, despite all reasonable steps in the design of the plant, extreme weather or other incidents are liable, in the view of the Regulator, to increase the odour impact at receptors, the Operator should take appropriate and timely action, as agreed with the Regulator, to prevent further annoyance (these agreed actions will be defined either in the Permit or in an odour management statement).

4 Where odour generating activities take place in the open, (or potentially odorous materials are stored outside) a high level of management control and use of best practice will be expected.

5 Where an installation releases odours but has a low environmental impact by virtue of its remoteness from sensitive receptors, it is expected that the Operator will work towards achieving the standards described in this Note, but the timescales allowed to achieve this might be adjusted according to the perceived risk.

2.3 Management

Within IPPC, an effective system of management is a key technique for ensuring that all appropriate pollution prevention and control techniques are delivered reliably and on an integrated basis.

The Regulators strongly support the operation of formal environmental management systems (EMSs). An Operator with such a system will not only find it easier to meet the BAT requirements for management of the installation but also many of the technical/regulatory requirements listed in other Sections of this Guidance.

The Regulators recommend either certification to the ISO 14001 standard or registration under EMAS (EC Eco Management and Audit Scheme) (OJ L114, 24/04/01). Both certification and registration provide independent verification that the EMS conforms to an auditable standard. EMAS now incorporates ISO 14001 as the specification for the EMS element, and the Regulators consider that overall EMAS has a number of other benefits over ISO14001 - including a greater focus on environmental performance, a greater emphasis on legal compliance, and a public environmental statement. For further details about ISO 14001 and EMAS contact British Standards Institute (BSI) or the Institute of Environmental Management and Assessment (IEMA), respectively.

Whilst an effective EMS will help the Operator to maintain compliance with specific regulatory requirements and manage all significant environmental impacts, this section of the Guidance identifies only those EMS requirements that are not specifically covered elsewhere in the document. This Section should not, therefore, be taken to describe all of the elements of an effective environmental management system. The requirements below are considered to be BAT for IPPC, but they are the same techniques required by a formal EMS and so should be capable of delivering wide environmental benefits.

The European Commission has also set out its views on BAT and Environmental Management Systems in the form of standard text which will be included in all new and updated BREFs.

Indicative BAT requirements for management techniques (Sheet 1 of 3)

Operations and maintenance

1 Effective operational and maintenance systems should be employed on all aspects of the process whose failure could impact on the environment, in particular there should be:

- documented procedures to control operations that may have an adverse impact on the environment
- a defined procedure for identifying, reviewing and prioritising items of plant for which a preventative maintenance regime is appropriate
- documented procedures for monitoring emissions or impacts
- a preventative maintenance programme covering all plant, whose failure could lead to impact on the environment, including regular inspection of major ‘non productive’ items such as tanks, pipework, retaining walls, bunds ducts and filters

2 The maintenance system should include auditing of performance against requirements arising from the above and reporting the result of audits to top management.

Indicative BAT requirements for management techniques (Sheet 2 of 3)

Competence and training

3 Training systems, covering the following items, should be in place for all relevant staff which cover

- awareness of the regulatory implications of the Permit for the activity and their work activities;
- awareness of all potential environmental effects from operation under normal and abnormal circumstances
- awareness of the need to report deviation from the Permit
- prevention of accidental emissions and action to be taken when accidental emissions occur

4 The skills and competencies necessary for key posts should be documented and records of training needs and training received for these post maintained.

5 The key posts should include contractors and those purchasing equipment and materials;

6 The potential environmental risks posed by the work of contractors should be assessed and instructions provided to contractors about protecting the environment while working on site.

7 Where industry standards or codes of practice for training exist (e.g. WAMITAB) they should be complied with.

Accidents/incidents/non-conformance

8 There should be an accident plan as described in **Section 2.8** which:

- identifies the likelihood and consequence of accidents
- identifies actions to prevent accidents and mitigate any consequences

9 There should be written procedures for handling, investigating, communicating and reporting actual or potential non-compliance with operating procedures or emission limits.

10 There should be written procedures for handling, investigating, communicating and reporting environmental complaints and implementation of appropriate actions.

11 There should be written procedures for investigating incidents, (and near misses) including identifying suitable corrective action and following up

12 The company should conduct audits, at least annually, to check that all activities are being carried out in conformity with the above requirements. Preferably, these should be independent.

13 The company should report annually on environmental performance, objectives and targets, and future planned improvements. Preferably, these should be published environmental statements.

Organisation

14 The following are indicators of good performance which may impact on the Regulator’s resources, but not all will necessarily be insisted upon as Permit conditions:

15 The company should adopt an environmental policy and programme which:

- includes a commitment to continual improvement and prevention of pollution;
- includes a commitment to comply with relevant legislation and other requirements to which the organisation subscribes; and
- identifies, sets, monitors and reviews environmental objectives and key performance indicators independently of the Permit.

Indicative BAT requirements for management techniques (Sheet 3 of 3)

16 The company should have demonstrable procedures (eg. written instructions) which incorporate environmental considerations into the following areas:

- the control of process and engineering change on the installation;
- design, construction and review of new facilities and other capital projects (including provision for their decommissioning);
- capital approval; and
- purchasing policy.

17 The company should operate a formal Environmental Management System. Preferably, this should be a registered or certified EMAS/ISO 14001 system (issued and audited by an accredited certification body).

18 The company should have a clear and logical system for keeping records of, amongst others:

- policies
- roles and responsibilities
- targets
- procedures
- results of audits
- results of reviews

2.4 Raw Materials

This section covers the use of raw materials and water, and the techniques for both minimising their use and minimising their impact by selection. (Energy and fuels are covered under **Section 2.7**, Energy).

As a general principle, the Operator will need to demonstrate the measures taken to:

- reduce the usage of all raw materials and intermediates (**Section 2.4.2**)
- substitute less harmful materials, or those which can be more readily abated and when abated lead to substances that are more readily dealt with (**Section 2.4.1**)
- understand the fate of by-products and contaminants and their environmental impact (**Section 2.4.2**)

2.4.1 Raw materials selection

This section looks at the selection and substitution of raw materials and the following section, **Section 2.4.2**, describes the techniques to minimise their use.

The process of selecting raw materials can present an opportunity to control emissions at source so, in this regard, the range of possible raw material options should be carefully examined.

An Application for a Permit should contain a list of the materials in use which have potential for significant environmental impact, together with the following associated information:

- the chemical composition of the materials, where relevant;
- the quantities used;
- the fate of the material in the installation (i.e. approximate percentages to each environmental medium and to the products);
- the environmental impact potential, where known (e.g. degradability, bioaccumulation potential, toxicity to relevant species);
- any reasonably practicable alternative raw materials that may have a lower environmental impact (including, but not limited to, any alternatives described in the BAT requirements below) on the substitution principle;
- and justification for the continued use of any substance for which there is a less hazardous alternative (e.g. on the basis of impact on product quality) to show that the proposed raw materials are therefore BAT.

In the chemical sectors, raw material selection is often determined by the design of the process but, in manufacturing a particular product, there is sometimes a choice between processes - between those which use raw materials of different potential for environmental harm, which have different product yields, and which generate different types or amount of wastes. As a general rule, the process with the least environmental impact should be chosen, although it should be recognised that the choice may be constrained, for example, by the integration of processes on a complex site.

The purity of raw materials will often affect yields and the presence of impurities may result in the need for excessive recycle and/or recovery operations with consequent higher energy consumption. The use of high purity raw materials will generally minimise the environmental impact of that process but may have adverse consequences on their own upstream production; for example, the use of oxygen rather than air may have benefits in reduced emissions to air but these have to be weighed against the energy requirements for air separation, as well as any cost implications.

Catalysts can result in large improvements in reaction selectivity and conversion rates, resulting in lower waste formation and energy usage. Reactions often proceed at lower temperatures and pressures when catalysed. The development of new and improved catalysts is important in many sectors of the industry and, in addition to their use in new processes, they can sometimes be retrofitted to improve the environmental and economic performance of existing installations (e.g. the replacement of potassium-based by caesium-based catalysts in sulphuric acid manufacture). The activity of fixed catalysts usually declines with time and where this has an effect on emissions, the optimum time for regeneration or replacement should be based on environmental performance rather than economic grounds. Some catalysts are toxic and it is necessary to control their dispersion, recovery and reuse or disposal; where a choice exists, the least polluting catalyst should be selected.

Solvents vary widely in their environmentally harmful properties, for example, in toxicity, stratospheric ozone depletion potential (ODP), photochemical ozone creation potential (POCP) and in their contribution to global climate change. Where possible, they should be selected to be of low environmental impact.

The use of gaseous fuels rather than heavy fuel oils is generally to be preferred as they are more easily desulphurised, the formation of nitrogen oxides in combustion equipment is more easily reduced and there is less tendency for fouling.

Indicative BAT requirements for raw materials selection

1 The Operator should maintain a list of raw materials and their properties as noted above.

2 The Operator should have procedures for the regular review of new developments in raw materials and for the implementation of any suitable ones with an improved environmental profile.

3 The Operator should have quality-assurance procedures for controlling the impurity content of raw materials.

4 The Operator should complete any longer-term studies needed into the less polluting options and should make any material substitutions identified.

2.4.2 Waste minimisation audit (minimising the use of raw materials)

The options for waste recovery and recycling are covered in **Section 2.6**. Waste avoidance/ minimisation, and the use of clean technologies, is a theme which runs throughout **Section 2.1** and **Section 2.2**. This section deals with the systematic approach to look for other opportunities.

Waste minimisation can be defined simply as: *“a systematic approach to the reduction of waste at source, by understanding and changing processes and activities to prevent and reduce waste”.*

A variety of techniques can be classified under the term waste minimisation, from basic housekeeping through statistical measurement, to application of clean technologies.

In the context of waste minimisation and this Guidance, waste relates to the inefficient use of raw materials and other substances at an installation. A consequence of waste minimisation will be the reduction of gaseous, liquid and solid emissions.

Key operational features of waste minimisation will be:

- the ongoing identification and implementation of waste prevention opportunities
- the active participation and commitment of staff at all levels including, for example staff suggestion schemes
- monitoring of materials' usage and reporting against key performance measures

For the primary inputs to activities which are themselves waste activities, eg. incineration, the requirements of this section may have been met "upstream" of the installation. However, there may still be arisings that are relevant.

See the **Waste minimisation and raw materials efficiency references** for detailed information, guides and case studies on waste minimisation techniques.

Indicative BAT requirements for waste minimisation audits
Identify the raw and auxiliary materials, other substances that are proposed for use.

1 The Operator should carry out a waste minimisation audit at least every 4 years. If an audit has not been carried out in the 2 years prior to submission of the Application for a Permit and the details made known at the time of that application, then the first audit shall take place within 2 years of the issue of the Permit. The methodology used and an action plan for reducing the use of raw materials should be submitted to the Regulator within 2 months of completion of the audit. The audit should be carried out as follows:

The Operator should analyse the use of raw materials, assess the opportunities for reductions and provide an action plan for improvements using the following three essential steps

- process mapping
- materials mass balance
- action plan

The use and fate of raw materials and other materials, including by-products, solvents and other support materials, such as fuels, catalysts and abatement agents, should be mapped onto a process flow diagram (see the **Waste minimisation and raw materials efficiency references**). This should be achieved by using data from the raw materials inventory and other company data as appropriate. Data should be incorporated for each principal stage of the operation in order to construct a mass balance for the installation.

2 Using this information, opportunities for improved efficiency, changes in process and waste reduction should be generated and assessed. An action plan should then be prepared for implementing improvements to a timescale approved by the Regulator.

2.4.3 Water use

Water is used in most Inorganics installations for cooling, for process use and for cleaning.

Where water is needed for cooling, its use should first be minimised by maximising heat transfer between process streams is also more energy efficient. Water should normally be used in recirculating systems with indirect heat exchangers and a cooling tower rather than a once through system. This avoids most of the heat transfer to the aquatic environment and reduces risks of undetected contamination. The quantity of treatment chemicals required is likely to be reduced. However, a water make-up treatment plant and a concentrated purge stream from the system are likely to be necessary. Where water is used in a once through cooling system, additional precautions and treatment will be required to minimise the risk of emissions of pollutants to the receiving of water.

Air cooling can be used in place of water where the characteristics of the process permit, but it uses energy in the fans and may be noisy in operation.

In the choice and design of cooling systems, it should be noted that the efficiency of cooling can have a significant effect on the release of uncondensed VOCs or other volatile compounds. An increase of a few degrees in condensation temperature may result in a multiple increase in losses. This subject is treated in detail in the Cooling BREF (**Ref 1**).

Water may be used in direct contact with process materials for either scrubbing or quench cooling. In most cases the water can be recirculated after stripping out the absorbed substances. A purge stream is normally required to avoid the build-up of contaminants and to remove water that is produced in the process. This will need treatment before discharge, although in some cases it may be used in another process.

Water used for cleaning can be reduced by a number of techniques, e.g. by using dry methods where possible and spray cleaning rather than whole vessel filling. Water should be reused wherever possible and a hierarchy of sources and opportunities for reuse may be established using pinch analysis.

Reasons for reducing water use

Water use should be minimised as part of BAT for the reduction of emissions to water and it should also be commensurate with the prudent use of water as a natural resource.

Reducing water use is normally a valid environmental (and economic) aim in itself, but any water passing through an industrial process is generally degraded so there will usually be an increase in pollutant load. The benefits to be gained from reducing water input include:

- reducing the size of (a new) treatment plant, thereby supporting the BAT cost-benefit justification of better treatment;
- cost savings where water is purchased from another party;
- cost savings where water is disposed of to another party;
- associated benefits within the process, such as reduced energy requirements for heating and pumping, and reduced dissolution of pollutants leading in turn to reduced sludge generation in the effluent treatment plant (and consequent disposal costs).

The use of a simple mass balance for water use should help to reveal where reductions can be made.

Advice on cost-effective measures for minimising water can be found in the **Water efficiency references:**.

Indicative BAT requirements for minimisation of water use (Sheet 1 of 2)

1 The Operator should carry out a regular review of water use (water efficiency audit) at least every 4 years. If an audit has not been carried out in the 2 years prior to submission of the application and the details made known at the time of the application, then the first audit should take place within 2 years of the issue of the Permit.

- Flow diagrams and water mass balances for the activities should be produced.
- Water-efficiency objectives should be established, with constraints on reducing water use beyond a certain level being identified (which usually will be usually installation-specific).
- Water pinch techniques should be used in the more complex situations such as chemical plant, to identify the opportunities for maximising reuse and minimising use of water (see the **Water efficiency references:**).

2 Within 2 months of completion of the audit, the methodology used should be submitted to the Regulator, together with proposals for a time-tabled plan for implementing water reduction improvements for approval by the Regulator.

Indicative BAT requirements for minimisation of water use (Sheet 2 of 2)

3 The following general principles should be applied in sequence to reduce emissions to water:

- Water-efficient techniques should be used at source where possible
- Water should be recycled within the process from which it issues, by treating it first if necessary. Where this is not practicable, it should be recycled to another part of the process that has a lower water-quality requirement
- In particular, if uncontaminated roof and surface water cannot be used in the process, it should be kept separate from other discharge streams, at least until after the contaminated streams have been treated in an effluent treatment system and been subject to final monitoring.

4 Measures should be in place to minimise the risk of contamination of surface waters or groundwater by fugitive releases of liquids or solids (see **Section 2.2.5**).

5 The water-quality requirements associated with each use should be established, and the scope for substituting water from recycled sources identified and input into the improvement plan.

Less contaminated water streams, such as cooling waters, should be kept separate from more contaminated streams where there is scope for reuse - though possibly after some form of treatment.

Most wastewater streams will however need some form of treatment (see **Section 2.2.2** for techniques) but for many applications, the best conventional effluent treatment can produces a water that is usable in the process directly or when mixed with fresh water. Though treated effluent quality can vary, it can often be recycled selectively - used when the quality is adequate, discharged when the quality falls below that which the system can tolerate.

6 In particular, the cost of membrane technology continues to reduce, and they can be applied to individual process streams or to the final effluent from the effluent treatment plant, as appropriate. In some applications in some Sectors, they can supplement (or possibly completely replace) the ETP plant so that most water is recyclable and there is a greatly reduced effluent volume. Where the remaining, possibly concentrated, effluent stream is sufficiently small - and particularly where waste heat is available - further treatment by evaporation can lead to zero aqueous effluent. Where appropriate, the Operator should assess the costs and benefits of using membrane techniques to minimise water usage and effluent discharge.

7 Water usage for cleaning and washing down should be minimised by:

- vacuuming, scraping or mopping in preference to hosing down;
- reusing wash water (or recycled water) where practicable;
- using trigger controls on all hoses, hand lances and washing equipment.

8 Fresh water consumption should be directly measured and recorded regularly at every significant usage point - ideally on a daily basis.

2.5 Waste Handling

As the response to the requirement for an emissions inventory in the Application for a Permit, the nature and source of the waste from each activity should be listed in detail - though where there are a very large number of relatively small streams, some aggregation of similar and relatively insignificant waste streams may be appropriate.

2.5.1 Nature of Inorganics sector Wastes

The wastes produced by the sector are specific to the individual processes and are included in the process descriptions in **Section 2.1**. They can be classified into types as follows:

- by-products for which no internal use or external sale is available;
- residues from separation processes such as distillation;
- catalysts which have declined in performance and require replacement;
- filter cake, activated carbon, ion exchange resins, molecular sieves and other treatment materials;
- sludges from waste water treatment;
- emptied containers and packaging;
- maintenance and construction materials.

The key pollutants likely to be present can be derived from knowledge of the process, materials of construction, corrosion/erosion mechanisms and materials related to maintenance, validated as necessary by the appropriate analytical techniques. The presence of substances created by abnormal operation should be identified, since process abnormalities can carry through substances into the waste that are not normally present.

2.5.2 Handling and Storage of Wastes

A system should be maintained to record the quantity, nature, origin and where relevant, the destination, frequency of collection, mode of transport and treatment method of any waste which is disposed of or recovered. Records must be maintained of any waste sent off-site (Duty of Care).

All substances produced by the installation’s activities and disposed of to land or away from the site, should be handled and conveyed so as to prevent spillage, dust release and the generation of odours.

Wherever practicable, waste should be segregated and the disposal route identified (which should be as close to the point of production as practicable). Dedicated storage areas should be located away from watercourses and sensitive boundaries (i.e. adjacent to areas of public use) and protected against vandalism. Storage areas should be clearly marked, containers should be clearly labelled, and the maximum capacity of storage areas should be stated and not exceeded. The maximum storage period for containers should also be specified, and there should be in place procedures to prevent cross-contamination of wastes and the mixing of incompatible materials.

Liquids and sludges should be stored in tanks or covered containers in a secure bunded area pending disposal and, where spillage could occur, the plant layout should be such that any spillage can be prevented from entering any drainage system and can be collected. Containers should be regularly inspected and procedures should be in place to deal with damaged or leaking containers.

Specialist storage facilities should be provided for substances which are flammable, sensitive to heat or light, or have other special hazards. Incompatible waste types should be kept separate, and storage of wastes of particular environmental sensitivity should be avoided as far as possible.

Indicative BAT requirements for waste handling
Characterise and quantify each waste stream and describe the proposed measures for waste management, storage and handling.

1 A system should be in place and maintained which records the quantity, nature and origin of any waste that is disposed of or recovered - and also, where relevant, the destination, frequency of collection, mode of transport and treatment method for those wastes.

2 Wastes should be segregated wherever practicable, and the disposal routes identified. Disposal should be as near to the point of generation as is practicable.

3 Records should be maintained of any waste sent off-site (Duty of Care).

4 Appropriate steps should be taken to prevent all emissions from waste storage and handling (e.g. liquid or solid spillage, dust or VOC emission, and odour) (see **Section 2.2.4**, **Section 2.2.5** and **Section 2.2.6**).

2.6 Waste recovery or disposal

The Regulations require the Regulator, in setting Permit conditions, to take account of certain general principles, including that the installation in question should be operated in such a way that “waste production is avoided in accordance with Council Directive 75/442/EEC on waste; and where waste is produced it is recovered, or where this is technically or economically impossible it is disposed of, while avoiding or reducing the impact on the environment”. The objectives of the National Waste Strategies should also be considered.

Waste avoidance (minimisation) at source is addressed in detail in **Section 2.1** and related issues are addressed in the sections on abatement techniques (see **Section 2.2**). The specific requirement for a waste minimisation audit is noted in **Section 2.4.2**.

To meet these requirements, Operators should provide the Regulator with the information requested in point 2 below.

All wastes should be reviewed against this approach as there are opportunities and problems particular to each process. Some disposal options for particular processes are indicated in **Section 2.1**, but some generic Chemical sector conclusions can be drawn.

Waste minimisation is addressed in other sections of this Note and there are reference documents produced by, for example, the Institution of Chemical Engineers. Minimisation begins with the choice of process chemistry to give the optimum stoichiometry. Catalysts can often increase the product yield by improving conversion and selectivity.

Wastes can sometimes be recycled into the process or may be used in another process either within the installation or sold to another company for use. For example, waste solvent may not be pure enough for direct reuse but may be satisfactory for a less demanding process. Such outlets may justify expenditure to extract further useful materials from distillation residues and mixed fractions. Waste exchanges and Trade Associations may be helpful in locating productive outlets.

Scrubbing liquids such as ethanolamines are usually recovered and recycled on site, but may require further treatment if they become degraded. Recovery, off-site by the supplier if necessary,is preferred to destruction.

The use of catalysts is particularly significant. Some can be regenerated in place but most need removal and replacement. Many are based on precious metals and it is economic to recover these, usually by return to the supplier, but every effort should be made to recycle other catalysts even where the economics are less attractive.

Many wastes have a useful thermal value and this can be realised by burning under controlled conditions. Some gases like hydrocarbons are commonly used as fuel (though pollutants such as sulphur compounds should be removed before combustion) but other waste gases such as hydrogen cyanide, are best burned on-site under conditions appropriate to their hazardous nature.

Whilst the occasional flaring of gaseous wastes may be essential for safety purposes, it does not provide good control of combustion and it does not allow recovery of heat nor abatement of polluting emissions. Flaring should not be a preferred method of routine disposal of gaseous wastes. See **Section 2.2.1** for further details.

Where recovery or chemical treatment of liquid wastes is not feasible, other than in a few special cases, they should not be disposed to land. Thermal destruction is the next preferred alternative, and this may involve one of the oxidation techniques outlined in **Section 2.2.5**. of which incineration is the most common. A correctly designed and operated incinerator ensures a high degree of controlled combustion, allows recovery of heat and abatement of any polluting emissions which may be formed. For example, halogenated wastes need to be destroyed under waste incineration conditions, with scrubbing of the flue gases to remove acid pollutants.

Landfill may be suitable for a limited number of wastes which are non-polluting or are solidified or encapsulated to prevent leaching of contaminants. For example, some metal compounds when treated with lime are highly insoluble. Landfill of wastes from this sector should only be contemplated after all other alternatives have been thoroughly examined and rejected.

Indicative BAT requirements for waste recovery or disposal
Describe and justify how each waste stream is proposed to be disposed of.

1 Waste should be recovered, unless it is technically or economically impractical to do so.

2 Where waste must be disposed of, the Operator should provide a detailed assessment identifying the best environmental options for waste disposal - unless the Regulator agrees that this is unnecessary. For existing disposal activities, this assessment may be carried out as an improvement condition to a timescale to be approved by the Regulator.

2.7 Energy

BAT for energy efficiency under the PPC Regulations will be satisfied provided the Operator meets the following conditions:

either

- the Operator meets the basic energy requirements in Section 2.7.1 and Section 2.7.2 below and is a participant to a Climate Change Agreement (CCA) or a Direct Participant Agreement (DPA) within the Emissions Trading Scheme.

or

- the Operator meets the basic energy requirements in Section 2.7.1 and Section 2.7.2 below and the further sector-specific energy requirements in Section 2.7.3 below.

Note that even where a Climate Change Agreement or Direct Participant Agreement is in place, this does not preclude the consideration of energy efficiency (including those identified in Section 2.7.3) as part of an integrated assessment of BAT where they impact on other emissions, e.g. where:

- the choice of fuel impacts upon emissions other than carbon, e.g. sulphur in fuel
- the minimisation of waste by waste-to-energy does not maximise energy efficiency, e.g. by Combined Heat and Power (CHP)
- the most energy-intensive abatement leads to the greatest reduction in other emissions

Further guidance is given in the guidance note **H2 Energy efficiency for IPPC**.

2.7.1 Basic energy requirements (1)

The BAT requirements of this section are basic low-cost energy standards that apply whether or not a CCA or DPA is in force for the installation.

Indicative BAT requirements for basic energy requirements (1):
Provide a breakdown of the energy consumption and generation by source and the associated environmental emissions.

1 The Operator should provide the energy consumption information, shown in the table below, in terms of delivered energy and also, in the case of electricity, converted to primary energy consumption. For the public electricity supply, a conversion factor of 2.6 should be used. Where applicable, the use of factors derived from on-site heat and/or power generation, or from direct (non-grid) suppliers should be used. In the latter cases, the Operator should provide details of such factors. Where energy is exported from the installation, the Operator should also provide this information. All this information should be submitted in the application (in England and Wales the H1 software tool should be used to produce this information). The Operator should also provide energy flow information (such as “Sankey” diagrams or energy balances) showing how the energy is used throughout the process.

2 The Operator should provide the following Specific Energy Consumption (SEC) information. Define and calculate the SEC of the activity (or activities) based on primary energy consumption for the products or raw material inputs that most closely match the main purpose or production capacity of the installation. Provide a comparison of SEC against any relevant benchmarks available for the sector. (See BREF and Energy Efficiency Guidance)

Indicative BAT requirements for basic energy requirements (1):
Provide a breakdown of the energy consumption and generation by source and the associated environmental emissions.

3 The Operator should provide associated environmental emissions. This is dealt with in the Operator’s response to the emissions inventory using the H1 software tool.

Table 2.8: Example breakdown of delivered and primary energy consumption

Energy source	Energy consumption		
	Delivered, MWh	Primary, MWh	% of total
Electricity*			
Gas			
Oil			
Other (Operator to specify)			

* specify source.

* specify source.

2.7.2 Basic energy requirements (2)

The BAT requirements of this section are basic low-cost energy standards that apply whether or not a CCA or DPA is in force for the installation.

Indicative BAT requirements for basic energy requirements (2) (Sheet 1 of 2)
Describe the proposed measures for improvement of energy efficiency.

1 **Operating, maintenance and housekeeping measures** should be in place in the following areas. Indicative checklists of appropriate measures are provided in Appendix 2 of the guidance note **H2 Energy efficiency for IPPC**, where relevant:

- air conditioning, process refrigeration and cooling systems (leaks, seals, temperature control, evaporator/condenser maintenance)
- operation of motors and drives
- compressed gas systems (leaks, procedures for use)
- steam distribution systems (leaks, traps, insulation)
- space heating and hot-water systems
- lubrication to avoid high-friction losses
- boiler maintenance, e.g. optimising excess air
- other maintenance relevant to the activities within the installation

2 **Basic, low cost, physical techniques** should be in place to avoid gross inefficiencies. These should include insulation, containment methods, (such as seals and self-closing doors), and avoidance of unnecessary discharge of heated water or air (e.g. by fitting simple control systems such as timers and sensors).

Indicative BAT requirements for basic energy requirements (2) (Sheet 2 of 2)
Describe the proposed measures for improvement of energy efficiency.

3 **Energy-efficient building services** should be in place to deliver the requirements of the Building Services section of the guidance note **H2 Energy efficiency for IPPC**. For energy-intensive industries these issues may be of minor impact and should not distract effort from the major energy issues. They should nonetheless find a place in the programme, particularly where they constitute more than 5 percent of the total energy consumption.

4 **Energy management techniques** should be in place, according to the requirements of Section 2.3 noting, in particular, the need for monitoring of energy flows and targeting of areas for reductions.

5 **An energy efficiency plan** should be provided that:

- identifies all techniques relevant to the installation, including those listed above and in Section 2.7.3, that are applicable to the installation
- estimates the CO_2 savings that would be achieved by each measure over its lifetime
- and, in the case where the activities are NOT covered by a CCA or DPA; provides information on the equivalent annual costs of implementation of the technique, the costs per tonne of CO_2 saved and the priority for implementation. A procedure is given in the Energy Efficiency Guidance Note.

6 An example format of the energy efficiency plan is shown in **Table 2.9**.

Table 2.9: Example format for energy efficiency plan

ALL APPLICANTS			ONLY APPLICANTS WITHOUT CCA		
Energy efficiency measure	CO_2 savings (tonnes)		Equivalent Annual Cost (EAC) £k	EAC/CO_2 saved £/tonne	Date for implementation
	Annual	lifetime			

Refer to Energy Efficiency Guidance Note for appraisal methodology. Where other appraisal methodologies have been used, state the method, and provide evidence that appropriate discount rates, asset life and expenditure (£/t) criteria have been employed.

The energy efficiency plan is required to ensure that the Operator has considered all relevant techniques. However, where a CCA or DPA is in place the Regulator will only enforce implementation of those measures in categories 1-3 above.

2.7.3 Further energy-efficiency requirements

Some large Inorganics processes are major users of heat and power and others produce energy from their exothermic reactions. For these there may be greater opportunities for optimising energy efficiency in comparison to the smaller installations in the sector and to many other industrial sectors.

The integrated nitrogenous fertilizer sites have the greatest scope for energy integration in the sector but there is a practical limit to the complexity of highly integrated systems which can be effectively operated. Knock-on difficulties can occur during sequential start up and during major upsets so the absolute maximum of process integration may not always produce the best environmental performance in practice. Opportunities for energy efficiency improvements are noted in the process descriptions in **Section 2.1**.

Indicative BAT requirements for further energy-efficiency requirements
Climate Change Agreement or Trading Agreement.

1 The following techniques should be implemented where they are judged to be BAT based on a cost/benefit appraisal according to the methodology provided in Appendix 4 of the Guidance Note **H2 Energy efficiency for IPPC**.

Energy supply techniques

2 The following techniques should be considered:
- use of Combined Heat and Power (CHP)
- generation of energy from waste
- use of less polluting fuels

3 The Operator should provide justification that the proposed or current situation represents BAT, irrespective of whether or not a CCA or DPA is in place, where there are other BAT considerations involved, eg.:
- the choice of fuel impacts upon emissions other than carbon dioxide, eg. sulphur dioxide;
- the potential for practical energy recovery from waste conflicts with energy efficiency requirements.

4 Where there is an on-site combustion plant other guidance is also relevant. For plants greater than 50MW, Operators should consult the IPC guidance on power generation (reference IPC S2 1.01 Combustion Processes: Large boilers and furnaces 50MW(th) and over and supplement IPC S3 1.01 Combustion Processes). Operators of plant of 20-50MW should consult the Local Authority Air Pollution Control guidance. On IPPC installations this guidance will be generally applicable to plant under 20MW also. (All are available from the **EA website**).

2.8 Accidents

This section covers accidents and their consequences. It is not limited to major accidents but includes spills and abnormal operation.

Some installations will also be subject to the Control of Major Accident Hazards Regulations 1999 (COMAH) (see **Appendix 2** for equivalent legislation in Scotland and Northern Ireland). IPPC and COMAH can sometimes overlap, and some systems and information may be usable for either regime.

The COMAH regime applies to major hazards, and for accident scenarios covered by COMAH, Operators may refer in the Application to any COMAH reports already held by the Regulator. However, the accident provisions under IPPC also cover those which are below the classification threshold for major accidents under COMAH, so Operators need to consider smaller accidents and abnormal operation scenarios as well. Guidance prepared in support of the COMAH Regulations (see the **COMAH guides**), may also help IPPC Operators in considering ways to reduce the risks and consequences of accidents - whether or not they are covered by the COMAH regime.

General management requirements are covered in **Section 2.3**. For accident management, there are three particular components:

- identification of the hazards posed by the installation/activity
- assessment of the risks (hazard x probability) of accidents and their possible consequences
- implementation of measures to reduce the risks of accidents, and contingency plans for any accidents that do occur

Indicative BAT requirements for accidents and abnormal operations (Sheet 1 of 3)
Describe the documented system that you propose to be used to identify, assess and minimise the environmental risks and consequence of accidents.

1 A formal structured accident management plan should be in place which covers the following aspects:

2 **A - Identification of the hazards** to the environment posed by the installation using a methodology akin to a Hazop study. Areas to consider should include, but should not be limited to, the following:

- transfer of substances (eg. filling or emptying of vessels);
- overfilling of vessels;
- emissions from plant or equipment (eg. leakage from joints, over-pressurisation of vessels, blocked drains);
- failure of containment (eg. physical failure or overfilling of bunds or drainage sumps);
- failure to contain firewaters;
- wrong connections made in drains or other systems;
- incompatible substances allowed to come into contact;
- unexpected reactions or runaway reactions;
- release of an effluent before adequate checking of its composition;
- failure of main services (eg. power, steam, cooling water);
- operator error;
- vandalism.

Indicative BAT requirements for accidents and abnormal operations (Sheet 2 of 3)
Describe the documented system that you propose to be used to identify, assess and minimise the environmental risks and consequence of accidents.

3 **assess the risks**. Having identified the hazards, the process of assessing the risks should address six basic questions:

- how likely are they to occur? (source frequency)
- what gets out and how much? (risk evaluation of the event)
- where does it end up? (predictions for the emission – what are the pathways and receptors?)
- what are the consequences? (consequence assessment – the effects on the receptors)
- what are the overall risks? (determination of the overall risk and its significance to the environment)
- what can prevent or reduce the risk? (risk management – measures to prevent accidents and/or reduce their environmental consequences)

4 The depth and type of assessment will depend on the characteristics of the installation and its location. The main factors to take into account are:

- the scale and nature of the accident hazard presented by the installation and the activities
- the risks to areas of population and the environment (receptors)
- the nature of the installation and complexity of the activities and the relative difficulty in deciding and justifying the adequacy of the risk-control techniques

5 **C - identification of the techniques necessary to reduce the risks.** The following techniques are relevant to most installations:

- there should be an up-to-date inventory of substances, present or likely to be present, which could have environmental consequences if they escape. This should include apparently innocuous substances that can be environmentally damaging if they escape (for example, a tanker of milk spilled into a watercourse can destroy its ecosystem). The Permit will require the Regulator to be notified of any significant changes to the inventory.
- procedures should be in place for checking and handling raw materials and wastes to ensure compatibility with other substances with which they may accidentally come into contact.
- storage arrangements for raw materials, products and wastes should be designed and operated to minimise risks to the environment.
- there should be automatic process controls backed-up by manual supervision, both to minimise the frequency of emergency situations and to maintain control during emergency situations. Instrumentation will include, where appropriate, microprocessor control, trips and process interlocks, coupled with independent level, temperature, flow and pressure metering and high or low alarms.
- physical protection should be in place where appropriate (eg. barriers to prevent damage to equipment from the movement of vehicles).
- there should be appropriate secondary containment (eg. bunds, catchpots, building containment).
- techniques and procedures should be in place to prevent overfilling of tanks - lliquid or powder - (eg. level measurement displayed both locally and at the central control point, independent high-level alarms, high-level cut-off, and batch metering).
- where the installation is situated in a flood plain, consideration should be given to techniques which will minimise the risk of the flooding causing a pollution incident or making one worse.
- security systems to prevent unauthorised access should be provided where appropriate.
- there should be formal systems for the logging and recording of all incidents, near-misses, abnormal events, changes to procedures and significant findings of maintenance inspections.
- there should be procedures for responding to and learning from incidents, near-misses, etc.

Indicative BAT requirements for accidents and abnormal operations (Sheet 3 of 3)
Describe the documented system that you propose to be used to identify, assess and minimise the environmental risks and consequence of accidents.

- the roles and responsibilities of personnel involved in incident management should be formally specified.
- clear guidance should be available on how each accident scenario might best be managed (eg. containment or dispersion, to extinguish fires or to let them burn).
- procedures should be in place to avoid incidents occurring as a result of poor communications between staff at shift change or during maintenance or other engineering work.
- safe shutdown procedures should be in place.
- communication channels with emergency services and other relevant authorities should be established, and available for use in the event of an incident. Procedures should include the assessment of harm following an incident and the steps needed to redress this
- appropriate control techniques should be in place to limit the consequences of an accident, such as isolation of drains, provision of oil spillage equipment, alerting of relevant authorities and evacuation procedures.
- personnel training requirements should be identified and training provided.
- the systems for the prevention of fugitive emissions are generally relevant (**Section 2.2.4** and **Section 2.2.5**) and in addition, for drainage systems:
  - procedures should be in place to ensure that the composition of the contents of a bund sump, or sump connected to a drainage system, are checked before treatment or disposal;
  - drainage sumps should be equipped with a high-level alarm or with a sensor and automatic pump to storage (not to discharge);
  - there should be a system in place to ensure that sump levels are kept to a minimum at all times;
  - high-level alarms and similar back-up instruments should not be used as the primary method of level control.
- duplicate or standby plant should be provided where necessary, with maintenance and testing to the same standards as the main plant;
- spill contingency procedures should be in place to minimise accidental release of raw materials, products and waste materials and then to prevent their entry into water.
- process waters, potentially contaminated site drainage waters, emergency firewater, chemically-contaminated waters and spillages of chemicals should be contained and, where necessary, routed to the effluent system and treated before emission to controlled waters or sewer. Sufficient storage should be provided to ensure that this can be achieved. Any emergency firewater collection system should take account of the additional firewater flows and fire-fighting foams, and emergency storage lagoons may be needed to prevent contaminated firewater reaching controlled waters (see the **Releases to water references**).
- consideration should be given to the possibility of containment or abatement of accidental emissions from vents and safety relief valves/bursting discs. Where this may be inadvisable on safety grounds, attention should be focused on reducing the probability of the emission.

2.9 Noise

Within this section “noise” should be taken to refer to noise or vibration which is detectable beyond the site boundary.

Noise is a feature of many Inorganics installations, particularly the larger ones, and there are some features specific to the sector.

The use of large machines such as compressors and pumps which are sometimes installed without enclosure can give rise to high noise levels. Rotary rather than reciprocating machines generally produce less vibration and pulsation and are widely installed for all except specialised very high pressure applications. Low noise designs should be chosen where available, and equipment installed in an enclosure where noise might be a problem. Particularly noisy machines where the noise is not constant (such as compactors or pelletisers) should be in noise control enclosures.

Combustion equipment such as furnaces and heaters can produce a low resonant sound detectable at a considerable distance, but this can be moderated by good design. Although less common in the Inorganics sector, flares are a particular source of noise and the use of flares should be limited to emergency conditions (for a variety of reasons in addition to noise). The noise is often associated with steam injection for smoke suppression, but good design of flares tips can lessen the need for high rates of steam injection and provide quieter operation.

The operation of safety valves and other release devices for high pressure systems can be extremely noisy. Where possible, but without compromising safety, suitable silencers can be fitted. The blow-off from boilers and air compressors, for example during start up, should be minimised and silencers should be provided.

Careful design of building layout and consideration of the proximity of potential receptors such as residential areas can sometimes avoid problems in operation.

Where noise issues are likely to be relevant, an Application for a Permit should provide information on the following: (for more details see **H3 Part 1 Noise**)

- the main sources of noise and vibration that will fall within the PPC installation, and also on infrequent sources of noise and vibration;
- the nearest noise-sensitive sites;
- any conditions or limits imposed under other regimes;
- the local noise environment;
- any environmental noise measurement surveys, modelling or other relevant noise measurements;
- any specific local issues and proposals for improvements;
- any proposals for improvements.

- the level of detail supplied being commensurate with the risk of noise-related annoyance at sensitive receptors.

Where an installation poses no risk of noise-related environmental impact because the activities are inherently quiet, a simple justification should suffice - and further information is unlikely to be required. However, it should be noted that absence of complaints does not necessarily imply that there is no underlying level of annoyance.

The PPC Regulations require installations to be operated in such a way that “all the appropriate preventative measures are taken against pollution, in particular through the application of BAT”. The definition of pollution includes “emissions that may be harmful to human health or the quality of the environment, cause offence to human senses or impair or interfere with amenities and other legitimate uses of the environment”. BAT, therefore, is likely to be similar in practice to the requirements of the statutory nuisance legislation - which requires the use of “best practicable means” to prevent or minimise noise nuisance.

In the case of noise, “offence to any human senses” can normally be judged by the likelihood of complaints, but in some cases it may be possible to reduce noise emissions still further at reasonable costs, and this may exceptionally therefore be BAT for noise emissions.

For advice on how noise- or vibration-related limits and conditions will be determined see **H3 Part 1 Noise**

Indicative BAT requirements for noise and vibration

Describe the main sources of noise and vibration (including infrequent sources); the nearest noise-sensitive locations and relevant environmental surveys which have been undertaken; and the proposed techniques and measures for the control of noise.

1 The Operator should employ basic good practice measures for the control of noise, including adequate maintenance of any parts of plant or equipment whose deterioration may give rise to increases in noise (for example, bearings, air handling plant, the building fabric, and specific noise attenuation kit associated with plant or machinery).

2 The Operator should employ such other noise control techniques necessary to ensure that the noise from the installation does not give rise to reasonable cause for annoyance, in the view of the Regulator. In particular, the Operator should justify where Rating Levels ($L_{Aeq,T}$) from the installation exceed the numerical value of the Background Sound Level ($L_{A90,T}$).

3 Further justification will be required should the resulting field rating level ($L_{AR,TR}$) exceed 50 dB by day and a facade rating level exceed 45 dB by night, with day being defined as 07:00 to 23:00 and night 23:00 to 07:00.

4 In some circumstances "creeping background" (i.e. creeping ambient) may be an issue. Where this has been identified in pre-application discussions or in previous discussions with the local authority, the Operator should employ such noise control techniques as are considered appropriate to minimise problems to an acceptable level within the BAT criteria.

5 Noise surveys, measurements, investigations (e.g. on sound power levels of individual items of plant) or modelling may be necessary for either new or for existing installations, depending upon the potential for noise problems. Where appropriate, the Operator should have a noise management plan as part of its management system.

2.10 Monitoring

This section describes monitoring and reporting requirements for emissions to all environmental media. Guidance is provided for selecting the appropriate monitoring methodologies, frequency of monitoring, compliance-assessment criteria and environmental monitoring.

2.10.1 Emissions monitoring

Indicative BAT requirements for emissions monitoring (Sheet 1 of 2)
Describe the proposed measures for monitoring emissions, and the frequency, measurement methodology and evaluation procedure proposed.

1 Monitoring should generally be undertaken during all phases of operation (i.e. commissioning, start-up, normal operation and shutting-down) unless the Regulator agrees that it is inappropriate.

2 Continuous monitoring and recording (or at least sampling in the case of water) are likely to be required under the following circumstances:

- Where the potential environmental impact is significant or the concentration of substance varies widely.
- Where a substance is abated continuous monitoring of the substance is required to show the performance of the abatement plant. For example continuous monitoring of dust is needed after a fabric filter to show the effectiveness of the filter and indicate when maintenance is needed, or sampling BOD from an effluent treatment plant.
- Where other control measures are required to achieve satisfactory levels of emission (e.g. material selection).

3 Where effective surrogates are available, they may be used with the agreement of the Regulator (and without prejudice to legal requirements) to minimise monitoring costs.

4 Where monitoring shows that substances are not emitted in significant quantities, it may be reasonable to reduce the monitoring frequency.

Monitoring and reporting of emissions to air

5 Where appropriate, periodic visual and olfactory assessment of releases should be undertaken to ensure that all final releases to air should be essentially colourless, free from persistent trailing mist or fume and free from droplets.

Monitoring and reporting of emissions to water and sewer

6 An analysis covering a broad spectrum of substances should be carried out to establish that all relevant substances have been taken into account for the purpose of setting emission limits. It should cover the substances listed in Schedule 5 of the Regulations unless it is agreed with the Regulator that they are not applicable. The need to repeat such tests will depend upon the variability in the process and, for example, the variability of raw materials.

Indicative BAT requirements for emissions monitoring (Sheet 2 of 2)
Describe the proposed measures for monitoring emissions, and the frequency, measurement methodology and evaluation procedure proposed.

7 Any substances found to be of concern, or any other individual substances to which the local environment may be susceptible and upon which the operations may impact, should also be monitored more regularly. This would particularly apply to the common pesticides and heavy metals. Using composite samples is the technique most likely to be appropriate where the concentration does not vary excessively.

8 In some sectors there may be releases of substances that are more difficult to measure and whose capacity for harm is uncertain, particularly when combined with other substances. "Whole effluent toxicity" monitoring techniques can therefore be appropriate to provide direct measurements of harm, for example, direct toxicity assessment. (See **Section 2.2.2**.)

Monitoring and reporting of waste emissions

9 For waste emissions, the following should be monitored and recorded:

- the physical and chemical composition of the waste
- its hazard characteristics
- handling precautions and substances with which it cannot be mixed

Monitoring of emissions to controlled waters should include (as a minimum) the measurement of the parameter listed in **Table 2.10** or appropriate surrogates.

Table 2.10: Effluent discharge monitoring requirements and primary methods

Parameter	Monitoring type / frequency	Method specification Ref.)
pH	Continuous	BS 1647-2:1984
Temperature	Continuous	Traceable to national standards
Flow	Continuous	BS 3680 series
COD/BOD	Flow weighted sample or composite samples, weekly analysis, reported as flow weighted monthly averages	
TOC	Continuous	
Turbidity	Continuous	
Dissolved oxygen	Continuous	
Oil	Daily or weekly (depending on risk or history)	

2.10.2 Environmental monitoring (beyond installation)

Indicative BAT requirements for environmental monitoring (beyond installation)
Describe the proposed measures for any environmental monitoring, and the frequency, measurement methodology and evaluation procedure proposed.

1 The Operator should consider the need for environmental monitoring to assess the effects of emissions to controlled water, groundwater, air or land, or emissions of noise or odour.

2 Environmental monitoring may be required, for example, when:
- there are vulnerable receptors
- the emissions are a significant contributor to an Environmental Quality Standard (EQS) that may be at risk
- the Operator is looking for departures from standards based on lack of effect on the environment;
- to validate modelling work.

3 The need should be considered for:
- groundwater, where it should be designed to characterise both quality and flow and take into account short- and long-term variations in both. Monitoring will need to take place both up-gradient and down-gradient of the site
- surface water, where consideration will be needed for sampling, analysis and reporting for upstream and downstream quality of the controlled water
- air, including odour
- land contamination, including vegetation, and agricultural products
- assessment of health impacts
- noise

4 Where environmental monitoring is needed, the following should be considered in drawing up proposals:
- determinands to be monitored, standard reference methods, sampling protocols
- monitoring strategy, selection of monitoring points, optimisation of monitoring approach
- determination of background levels contributed by other sources
- uncertainty for the employed methodologies and the resultant overall uncertainty of measurement
- quality assurance (QA) and quality control (QC) protocols, equipment calibration and maintenance, sample storage and chain of custody/audit trail
- reporting procedures, data storage, interpretation and review of results, reporting format for the provision of information for the Regulation

5 Guidance on air quality monitoring strategies and methodologies can be found in **Monitoring Guidance**.

2.10.3 Monitoring of process variables

Indicative BAT requirements for monitoring of process variables
Describe the proposed measures for monitoring those process variables that may have a significant effect on emissions.

Some process variables may affect the environment and these should be identified and monitored as appropriate. Examples might be:

- raw materials monitoring for contaminants where contaminants are likely and there is inadequate supplier information (see **Section 2.4.1**)
- plant efficiency where it has an environmental relevance
- abatement equipment performance (e.g. bag filter pressure drop)
- energy consumption across the plant and at individual points-of-use in accordance with the energy plan. Frequency – normally continuous and recorded
- fresh water use across the activities and at individual points-of-use should be monitored as part of the water-efficiency plan (see **Section 2.4.3**). Frequency – continuous and recorded

2.10.4 Monitoring standards (Standard Reference Methods)

The Environment Agency’s Monitoring Certification Scheme (MCERTS) - Background

For England and Wales, the Environment Agency has established its Monitoring Certification Scheme (MCERTS) to deliver quality environmental measurements. MCERTS provides for the product certification of monitoring systems (for example, instruments, analysers and equipment), the competency certification of personnel and the accreditation of laboratories under the requirements of European and International standards. MCERTS has been developed to reflect the growing requirements for regulatory monitoring to meet European and International standards. It brings together relevant standards into a scheme that can be easily accessed by key stakeholders, such as manufacturers, operators, regulators and test houses. Eventually, MCERTS will be extended to include all regulatory monitoring activities. Technical Guidance Notes M1 and M2 are key reference documents underpinning MCERTS for stack-emission monitoring.

The Agency has published MCERTS performance standards for continuous emissions monitoring systems (CEMs), ambient air quality monitoring systems (CAMs), the chemical testing of soils, water monitoring instrumentation and manual stack emissions monitoring. Other MCERTS standards are under development to cover portable emissions monitoring equipment, data acquisition and operators’ own arrangements, such as installation, calibration and maintenance of monitoring equipment.

The legal context of MCERTS

Some European Directives, such as the WID, specify that monitoring and related activities such as calibration must be performed to CEN standards or, if CEN standards are not available, to ISO, national or other international standards which provide data of a suitable quality. As MCERTS is based on international standards - primarily CEN standards - MCERTS is a means of demonstrating compliance with applicable standards. Furthermore, MCERTS for CEMs provides test data to demonstrate that the monitoring equipment meets the uncertainty specifications specified in, for example, Annex III of the WID, and therefore demonstrates compliance with the QAL1 requirements of a new standard, EN14181 as described in section 2.10.5.

MCERTS for CEMs

There are three elements to MCERTS for CEMs, which are:

- performance specifications for CEMs, drawn from international standards such as BS EN 12619 for total organic carbon (TOC);
- performance evaluation of CEMs, based on international standards including specific standards for CEMs (such as BS EN 12619), and test standards such as ISO 9169 and BS EN ISO/IEC 17025;
- product certification based on BS EN 45011.

Product certification assures that the manufacturing of CEMs is reproducible and that manufacturers take into account the impact of design changes to CEMs, assuring that any such changes to certified equipment do not degrade the performance below the MCERTS performance standards.

When selecting CEMs for plant, the certified range and determinands are important. For example, the CEMs for incinerators should have MCERTS certification for the determinands specified in the WID, as well as peripheral determinands such as oxygen and moisture if the CEMs measure emissions on a wet basis.

Regarding certified ranges, the range should not be greater than 1.5x the daily average ELV. For example, Table 2.10 below shows some examples of daily average emission limit values for key determinands and the applicable certified ranges. One exception to this rule is for hydrogen fluoride measurements, where the ELV is 1 mg/m3. In the case of HF, certified ranges up to 5 mg/m3 are acceptable. Certified ranges may be smaller than those based on a 1.5x multiplier of the ELV, since it has been demonstrated that CEMs proven over low ranges typically perform more than acceptably over high ranges. However, the converse is not necessarily true.

Table 2.11: Some applicable certified MCERTS ranges for incineration

Determinand	Daily average ELV (mg/m3)	Applicable minimum certified range (mg/m3)
Nitrogen oxides (as NO2)	200	300
Sulphur dioxide (SO2)	50	75
Carbon monoxide (CO)	50	75
Total dust	10	15
Hydrogen chloride (HCl)	10	15
Total organic carbon (TOC)	10	15

MCERTS and the German type-approval scheme

Germany operates a type-approval scheme for CEMs, whereby the testing is typically performed by TÜV laboratories and the approval is issued by the German Federal Environment Agency, the Umweltbundesamt (UBA). As there are similarities between MCERTS and the UBA schemes, UBA and the Agency cooperated in 2002 to align their respective schemes so that future testing and certification could provide for mutual recognition.

This mutual recognition also means that there is a fast-track scheme for equipment approved in one country and requiring certification in the other. The fast-track scheme means reduced performance evaluations due to mutual recognition of previous testing and certification. This has meant that some CEMs type-approved in Germany have been through the fast-track process and are now MCERTS certified as well.

CEN is currently developing an international standard for the performance evaluation and certification of CEMs. This standard is based on the aligned Anglo-German scheme.

MCERTS for manual stack monitoring

MCERTS for manual stack-emission monitoring is split into two components - the certification of personnel and the accreditation of organisations. MCERTS requires stack-emission monitoring organisations to be accredited by the United Kingdom Accreditation Service (UKAS) to ISO/IEC 17025 and the MCERTS performance standard for organisations. It provides an application of EN ISO/IEC 17025 in the specific field of measurement of air emissions from stacks and covers:

- ethical requirements for independence and environmental awareness;
- use of MCERTS certified personnel;
- selection of appropriate methods following international standards;
- method implementation;
- estimation of measurement uncertainty;
- use of appropriate equipment;
- planning of a sampling measurement campaign including provisions for a site review, risk assessment and a site-specific protocol;
- reporting of results;
- participation in proficiency-testing schemes.

The standard does not provide a sectorial application for analytical laboratory methods but does specify that any methods shall be accredited to the requirements of EN ISO/IEC 17025.

The MCERTS personnel competency standard defines the standards for certifying stack-emission monitoring personnel as competent based on experience, training and examination. The standard provides for two levels of personal competency, defined as L1 and L2. The first level, L1, covers the main requirements for all personnel wishing to demonstrate competence in stack emissions monitoring whilst the second level, L2, defines further requirements for managing emissions monitoring campaigns. There are also supplementary endorsements for each level, known as Technical Endorsements (TEs). There are currently five TEs in operation while a sixth is being developed to cover calibration requirements, as specified within EN 14181. The five current TEs are:

- TE1 - Particulate monitoring by isokinetic sampling techniques
- TE2 - Multi-phase sampling techniques
- TE3 - Gases/vapours by manual techniques
- TE4 - Gases/vapours by instrumental techniques
- TE5 - Particle-size fractionation by isokinetic sampling techniques

Monitoring personnel can be certified at either L1 or L2 whether or not they work within an MCERTS accredited organisation, although the latter must have MCERTS certified personnel at both the L1 and L2 levels. In order to comply with the requirements of EN 14181, all organisations performing SRMs on incinerators must be MCERTS accredited.

MCERTS and PPC applications for permits

The following should be described in the application, indicating which monitoring provisions comply with MCERTS requirements or where other arrangements have been made:

- monitoring methods and procedures (selection of Standard Reference Methods)
- justification for continuous monitoring or spot sampling
- reference conditions and averaging periods
- measurement uncertainty of the proposed methods and the resultant overall uncertainty
- criteria for the assessment of non-compliance with Permit limits and details of monitoring strategy aimed at demonstration of compliance

- reporting procedures and data storage of monitoring results, record keeping and reporting intervals for the provision of information to the Regulator
- procedures for monitoring during start-up and shut-down and abnormal process conditions
- drift correction calibration intervals and methods
- the accreditation held by samplers and laboratories or details of the people used and the training/ competencies

2.10.5 Quality assurance for CEMs

During 2004, CEN will publish a new standard entitled “EN 14181, Quality assurance of automated measuring systems (AMS)”. Shortly afterwards, the UK will adopt this standard as BS EN 14181, after which it must be used for all applicable installations. This standard will apply where EU Directives require it - for example, it will apply to all incineration and co-incineration installations which are within the scope of the WID. The scope of EN 14181 is restricted to quality assurance (QA) of the AMS, and does not include QA of the data collection and recording system of the plant.

The standard describes the procedures needed to assure that an AMS (known as CEMs in the UK) is capable of meeting the uncertainty requirements on measured values given by legislation - e.g. EU Directives or national legislation. EN 14181 defines three different quality assurance levels known as QAL 1, QAL 2 and QAL 3, plus an annual surveillance test (AST). The requirements of each of these are as follows:

QAL 1 - Uncertainty of the AMS before installation

- QAL 1 defines the procedures to demonstrate that an AMS will meet the uncertainty requirements specified in applicable EU Directives before the AMS is installed in the installation. For example, the WID specifies the uncertainty requirements in Annex III. The uncertainty of the AMS is determined using the procedures specified in another related standard, “BS EN ISO 14956, Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty.” This standard makes use of performance test data produced during type-testing, i.e. MCERTS test data.

QAL 2 - Quality assurance of installation

- QAL 2 describes a procedure to calibrate the AMS and determine the variability of the measured values obtained by an SRM (with a known uncertainty) which is suitable for the validation of an AMS following its installation. The SRM, in order to comply with the requirements of EU Directives such as Annex III of the WID, must be a CEN standard or, if there is no CEN standard available, an ISO, national or other international standard capable of providing data of an equivalent quality.
- The test organisation which performs the SRM must be accredited to BS EN ISO/IEC 17025 and the appropriate SRM standards, or recognised by the Regulator. In England and Wales, the Environment Agency is using MCERTS for manual stack monitoring as a means of recognition of competence.
- During QAL 2, the test organisation must take at least 15 concurrent measurements of the SRM and AMS spread over at least 3 days, with suitable intervals between each measurement. The data is then used to determine a regression line and calibration function, followed by a variability test to determine if the uncertainty of the AMS still complies with relevant Directive requirements following installation.

- If the AMS does not meet the uncertainty requirements specified in the relevant Directive, the operator must then take corrective action to remedy this. The Directive may require the QAL 2 test to be performed at defined times - For example, the WID requires the test to be performed every three years and after major services or other major changes. The latter includes changes of fuel: for example, if the calibration function was determined for a cement kiln burning a mixture of coal and secondary liquid fuel (SLF), a new calibration may be required if a new material (e.g. tyres) were used instead of the SLF.
- QAL 2 also defines a number of functional tests.

QAL 3 - Quality assurance during operation

- The QAL 3 procedure defines the necessary steps to demonstrate the required quality of the measurements during the normal operation of an AMS, by checking that the precision and zero and span characteristics are consistent with those determined during QAL 1.

Annual surveillance test (AST)

- The AST is a reduced QAL 2 test. The AST is designed to assure that the AMS continues to function correctly, that its performance remains valid and that the calibration function and variability remain as previously determined. In order to verify the calibration function, a qualified test organisation performs at least five repetitions of an SRM. If the calibration function is no longer valid, then a full QAL 2 test must be performed. The table below outlines the tests and checks required during the QAL 2 and AST procedures.

Table 2.1: Summary of QAL 2 and AST requirements

Activity	QAL 2		AST	
	Extractive AMS	Non-extractive AMS	Extractive AMS	Non-extractive AMS
Alignment and cleanliness		X		X
Sampling system	X		X	
Documentation and records	X	X	X	X
Serviceability	X	X	X	X
Leak test	X		X	
Zero and span check	X	X	X	X
Linearity			X	X
Interferences			X	X
Zero and span drift (Audit)			X	X
Response time	X	X	X	X
Report	X	X	X	X

Indicative BAT requirements for monitoring standards (Standard Reference Methods)
Describe the methods proposed for analysing emissions and for environmental monitoring.

1 As far as possible, Operators should ensure their monitoring arrangements comply with the requirements of MCERTS where available, for example using certified instruments and equipment, and using a stack testing organisation accredited to MCERTS standards. Where the monitoring arrangements are not in accordance with MCERTS requirements, the Operator should provide justification and describe the monitoring provisions in detail. See **www.mcerts.net** for future information on MCERTS and a listing of MCERTS equipment.

Sampling and analysis standards

2 Standards should be selected in the order of priority as given in the IPPC Bureau's Reference Document on the General Principles of Monitoring. This order is:

- Comitee Europeen de Normalisation (CEN)
- International Standardisation Organisation (ISO)

If the substance cannot be monitored using CEN or ISO standards then a method can be selected from any one of the following

- American Society for Testing and Materials (ASTM)
- Association Francaise de Normalisation (AFNOR)
- British Standards Institution (BSI)
- Deutsches Institute fur Normung (DIN
- United States Environmental Protection Agency (US EPA)
- Verein Deustcher Ingenieure (VDI)

If the substance cannot be monitored using any of the standards above then other methods may be adapted for use, following the requirements for validation in ISO 17025. For stack emission monitoring the following occupational methods may be adapted:

- Methods for the Determination of Hazardous Substances (MHDS) series published by the Health and Safety Executive (HSE)
- National Institute for Occupational Safety and Health (NIOSH)
- Occupational Safety and Health Administration (OSHA)

The intended application of the standard method must always be taken into account. For example, a CEN method may be less suitable than another less-rigorously validated standard method if the application is not one for which the CEN method was developed.

Operators should be expected to be able to demonstrate compliance with the above hierarchy and validate use of non-standard methods, in-house designed/developed methods, standard methods used outside their intended scope and modifications of standard methods to confirm that these methods are fit for purpose.

3 Further guidance on standards for monitoring gaseous releases relevant to IPC/IPPC is given in the **Monitoring Guidance**. A series of updated Guidance Notes covering this subject is being prepared. This guidance specifies manual methods of sampling and analysis that will also be suitable for calibration of continuous emission monitoring instruments. Further guidance relevant to water and waste is available from the publications of the Standing Committee of Analysts.

4 If in doubt the Operator should consult the Regulator.

2.11 Closure

The PPC Regulations require an Applicant to submit a site report, describing the condition of the site, as part of the application. Guidance on this is in Annex C of the Guide for Applicants (see **IPPC Part A(1) Installations: Guide for Applicants (England and Wales)**) or Guidance for SEPA Staff On Land and Groundwater Considerations for PPC Part A Installations (Scotland) (see **PPC Part A Installations: Guide for Applicants (Scotland)**).

Indicative BAT requirements for closure (Sheet 1 of 2)
Describe the proposed measures, upon definitive cessation of activities, to avoid any pollution risk and to return the site of operation to a satisfactory state (including measures relating to the design and construction of the installation, where appropriate).)

1 **Operations during the IPPC Permit**
Operations during the life of the IPPC Permit should not lead to any deterioration of the site if the requirements of the other sections of this and the specific-sector notes are adhered to. Should any instances arise which have, or might have, impacted on the state of the site, the Operator should record them along with any further investigation or ameliorating work carried out. This will ensure that there is a coherent record of the state of the site throughout the period of the IPPC Permit. This is as important for the protection of the Operator as it is for the protection of the environment. Any changes to this record should be submitted to the Regulator.

2 **Steps to be taken at the design-and-build stage of the activities**
Care should be taken at the design stage to minimise risks during decommissioning. For existing installations, where potential problems are identified, a programme of improvements should be put in place to a timescale agreed with the Regulator. Designs should ensure that:

- underground tanks and pipework are avoided where possible (unless protected by secondary containment or a suitable monitoring programme)
- there is provision for the draining and clean-out of vessels and pipework prior to dismantling
- lagoons and landfills are designed with a view to their eventual clean-up or surrender
- insulation is provided that is readily dismantled without dust or hazard
- materials used are recyclable (having regard for operational or other environmental objectives)

3 **The site-closure plan**
A site closure plan should be maintained to demonstrate that, in its current state, the installation can be decommissioned to avoid any pollution risk and return the site of operation to a satisfactory state. The plan should be kept updated as material changes occur. Common sense should be used in the level of detail, since the circumstances at closure will affect the final plans. However, even at an early stage, the closure plan should include:

- either the removal or the flushing out of pipelines and vessels where appropriate and their complete emptying of any potentially harmful contents
- plans of all underground pipes and vessels
- the method and resource necessary for the clearing of lagoons
- the method of ensuring that any on-site landfills can meet the equivalent of surrender conditions
- the removal of asbestos or other potentially harmful materials unless agreed that it is reasonable to leave such liabilities to future owners
- methods of dismantling buildings and other structures, see **Closure references** which gives guidance on the protection of surface and groundwater at construction and demolition-sites

Indicative BAT requirements for closure (Sheet 2 of 2)
Describe the proposed measures, upon definitive cessation of activities, to avoid any pollution risk and to return the site of operation to a satisfactory state (including measures relating to the design and construction of the installation, where appropriate).)

- testing of the soil to ascertain the degree of any pollution caused by the activities and the need for any remediation to return the site to a satisfactory state as defined by the initial site report

4 For existing activities, the Operator should complete any detailed studies, and submit the site-closure plan as an improvement condition to a timescale to be agreed with the Regulator but in any case within the timescale given in **Section 1.1** (Note that radioactive sources are not covered by this legislation, but decommissioning plans should be co-ordinated with responsibilities under the Radioactive Substances Act 1993.)

2.12 Issues for multi-operator Installations

In some cases it is possible that actions that benefit the environmental performance of the overall installation will increase the emissions from one Permit-holder's activities. For example, taking treated effluent as a raw water supply will probably slightly increase emissions from that activity, but could dramatically cut the total emissions from the whole installation.

Where you are not the only Operator of the installation, describe the proposed techniques and measures (including those to be taken jointly by yourself and other Operators) for ensuring the satisfactory operation of the whole installation

Indicative BAT requirements for installation wide issues
If you are not the only Operator of the installation, describe the proposed techniques and measures taken by you and the other Operators to ensure satisfactory environmental performance of the installation as a whole.

1 The Operator should consider possibilities for minimising environmental impact to the environment as a whole, by operating together with other Permit holders. Possibilities include:

- Communication procedures between the various Permit-holders; in particular those needed to ensure that the risk of environmental incidents is minimised.
- Benefiting from the economies of scale to justify the installation of a CHP plant.
- The combining of combustible wastes to justify a combined waste-to-energy/CHP plant.
- The waste from one activity being a possible feedstock for another.
- The treated effluent from one activity being of adequate quality to be the raw water feed for another activity.
- The combining of effluent to justify a combined or upgraded effluent-treatment plant.
- The avoidance of accidents from one activity that may have a detrimental knock-on effect on the neighbouring activity.
- Land contamination from one activity affecting another – or the possibility that one Operator owns the land on which the other is situated.

3 Emission benchmarks

3.1 Emissions inventory

The Regulations require the Applicant to describe the nature, quantities and sources of foreseeable emissions into each medium. This will be done by completing the inventory of emission and consumption in the H1 software tool. The information required is as follows.

Provide a table of significant emissions of substances (except noise, vibration, odour and heat which are covered in their respective sections) that will result from the proposals and should include, preferably in order of significance:

- substance (where the substance is a mixture, for example, VOCs or COD, separate identification of the main constituents or inclusion of an improvement proposal to identify them)
- source, including height, location and efflux velocity
- media to which it is released
- any relevant EQS or other obligations
- benchmark
- proposed emissions normal/max expressed, as appropriate for:
  - mass/unit time
  - concentration
  - annual mass emissions
- statistical basis (average, percentile etc.)
- notes covering the Operators confidence in his ability to meet the benchmark values
- if intermittent, the appropriate frequencies
- plant loads at which the data is applicable
- whether measured or calculated (the method of calculation should be provided)

The response should clearly state whether the emissions are current emission rates or those planned following improvements, and should cover emissions under both normal and abnormal conditions for:

- point-source emissions to surface water, groundwater and sewer
- waste emissions
- point-source emissions to air
- significant fugitive emissions to all media, identifying the proportion of each substance released that is due to fugitives rather than point-source releases
- abnormal emissions from emergency relief vents, flares and the like
- indirect and direct emission of carbon dioxide associated with energy consumed or generated

Emissions of carbon dioxide associated with energy use should be broken down by energy type and, in the case of electricity, by source, for example, public supply, direct supply or on-site generation. Where energy is generated on-site, or from a direct (non-public) supplier, the Operator should specify and use the appropriate factor. Standard factors for carbon dioxide emissions are provided in the guidance note **H2 Energy efficiency for IPPC**.

Where VOCs are released, the main chemical constituents of the emissions should be identified.

For waste, emissions relate to any wastes removed from the installation, or disposed of at the installation under the conditions of the Permit, for example, landfill. Each waste should have its composition determined and the amounts expressed in terms of cubic metres or tonnes per month. A suitable table on which to record this information is provided in the electronic version of this Guidance Note.

	Indicative BAT requirements for emission benchmarks Describe the nature, quantities and sources of foreseeable emissions into each medium (which will result from the techniques proposed in Section 2).
1	The Operator should compare the emissions with the benchmark values given in the remainder of this Section.
2	Where the benchmarks are not met, the Operator should revisit the responses made in Section 2 as appropriate and make proposals for improvements or justify not doing so as part of the BAT assessment.

3.2 Emission benchmarks

Introduction to emission benchmarks

Guidance is given below on release concentrations or mass release rates achievable for key substances using the best combination of techniques. These BAT-based benchmarks are not mandatory release limits and reference should be made to Section 1 and the Guide for Applicants regarding their use.

3.2.1 Emissions to air associated with the use of BAT

The emissions quoted below are daily averages based upon continuous monitoring during the period of operation. See **Section 3.2.6** for the standard conditions that should be applied. Care should always be taken to convert benchmark and proposed releases to the same reference conditions for comparison. To convert measured values to reference conditions, see the **Monitoring Guidance** for more information. The benchmarks given do not take sampling, analytical errors, or uncertainties into account. These will be considered when setting an ELV for a Permit.

Limits in Permits may be set for mean or median values over long or short periods. The periods and limits selected should reflect:

- the manner in which the emission may impact upon the environment
- likely variations which will arise during operation within BAT
- possible failure modes and their consequences
- the capabilities of the monitoring and testing system employed

Where emissions are expressed in terms of concentrations and where continuous monitors are employed, it is recommended that limits are defined such that:

- not more than one calendar monthly average during any rolling twelve month period shall exceed the benchmark value by more than 10%
- not more than one half hour period during any rolling 24 hour period shall exceed the benchmark value by more than 50% (for the purpose of this limit half hourly periods commence on the hour and the half hour)

Where spot tests are employed:

- the half hour limit above shall be applied over the period of the test
- the mean of three consecutive tests taken during a calendar year shall not exceed the benchmark value by more than 10%

This Guidance covers a very wide range of chemical processes and abatement techniques so the relevance of the benchmarks below will vary. Pollutants which have emission limit values (ELVs) set and particularly those for which monitoring is required, should be selected according to their potential for environmental impact. Although continuous monitoring should be undertaken wherever practicable, where the process is relatively small-scale or comprises batch production, periodic monitoring or critical-stage monitoring may be more appropriate.

Table 3.1: Emissions to air

Released substance	Benchmark value (mg/Nm^3) See Note (a)	Comments and basis for the benchmark. (Based on IPC S2 4.03 and S2 4.04 unless otherwise indicated)
Amonia	10 - 50	10 mg/Nm^3 for acid scrubbing (BREF), 30 for NH_3 plants, 10 - 50 for Fertilizer production (see Note (b))
Antimony	5	
Arsenic	1	
Benzene	5	
Beryllium	0.002	
Bromine	10	
Cadmium and cpds (as Cd)	0.05 - 0.1	0.05 mg/Nm^3 for cadmium processes, 0.1 for incineration
Carbon disulphide	5	
Carbon monoxide	100	
Chlorides (gaseous) (as HCl)	10	
Chlorine	10	See Note (c) for TiO_2 manufacture
Chlorine dioxide (as Cl)	10	
Chromium (III)	5	1 mg/Nm^3 when mixed with Cr^{VI} or a soluble Ni compound
Chromium (VI)	0.5 - 1	0.5 mg/Nm^3 when present as chromates of Ca, Sr, $Cr^{(III)}$ or Zn; 1mg/Nm^3 for all other $Cr^{(VI)}$ compounds
Cyanide dust (inorganic)	5	
Cyanogen chloride	1	
1,2-Dichloroethane	1 - 5	1mg/Nm^3 by incineration treatment (BREF))
Fluorides (gaseous) (as HF)	10	
Heavy metals (other than Hg and Cd)	1.5	Waste Incineration Directives
Hydrogen bromide	5	
Hydrogen chloride	10	
Hydrogen cyanide	2 - 5	
Hydrogen fluoride	5	
Hydrogen iodide	5	
Hydrogen sulphide	5	
Indium	1	
Iodine	10	
Lead and compounds (inorganic)	2	
Mercaptans and Organic sulphides (as methyl mercaptan)	2	

Table 3.1: Emissions to air

Released substance	Bench-mark value (mg/Nm^3) See Note (a)	Comments and basis for the benchmark. (Based on IPC S2 4.03 and S2 4.04 unless otherwise indicated)
Mercury and compounds (as Hg)	0.05	
Nickel and compounds	2 - 10	2 mg/Nm^3 for soluble Ni compounds
Nitrogen oxides (acid-forming as $N0_2$)	50 - 200	200 mg/Nm^3 for wet scrubbing, 50 for SCR
Nitrous oxide (N_2O)	200	NSCR
Particulate matter	5 - 20	See Note (b) for ammonium nitrate & phosphate production
Phosphine	1 - 5	1 mg/Nm^3 for small uses like semiconductor manufacture; 5mg/Nm^3 for larger-scale use or production.
Phosphorus oxides (as P_2O_5)	50	
Phosphorus oxychloride	10	
Phosphorus pentasulphide	5	
Phosphorus trichloride	10	
Platinum	0.002 - 1	0.002 mg/Nm^3 for soluble Pt compounds
Selenium	1	
Sulphur oxides (as $S0_2$)	50 - 100	50 mg/Nm^3 for wet alkaline scrubbing (c.f. 40 mg/Nm^3 achievable according to WW&WG Treatment BREF); 100 for semi-dry scrubbing. For H_2SO_4 plants see Note (d) below.
Tellurium	1	
Thallium	0.05	
VOC total Class A	20	See Note (e)
VOC Total Class B (expressed as carbon)	75	See Note (e)

- Note (a) - General conditions
- 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.
- Where the terms "as" or "expressed as" are used, a correction should be carried out using the ratio of the atomic or molecular weights of the substances, as appropriate.
- Releases should be essentially colourless, free from persistent mist or fume and free from droplets.
- Releases should not give rise to an offensive odour noticeable outside the site where the process is carried on.
-

Note (b) - Ammonium nitrate or ammonium phosphate fertilizers

The following ammonia and particulate levels are achievable in the specified parts of ammonium nitrate or phosphate production:

Ammonium nitrate or phosphate activity		Ammonia	Particulate matter (mg/ Nm^3)
Ammonium nitrate production	Prill towers and melt granulators	10	15 (excluding insolubles)
	Neutralisers/reactors	50	30
	Coolers and dryers	50	30
	Evaporators	50	15
Ammonium phosphate production		10	50

Note (c) - Titanium dioxide Directive

Titanium dioxide manufacture is subject to EC Directive 92/112/EEC which gives the following emission limits:

Substance		Emission limit value (mg/ Nm^3)
Chlorine (Chloride route)	- daily average	5
	- at any time	40
Sulphur oxides (Sulphate route) (as SO_2)		10 kg/t of TiO_2
Particulates	- main sources	50
	- minor sources	150

Note (d) - Sulphuric acid plants

Sulphuric acid plants can achieve the highest levels of conversion of SO_2 to SO_3 and sulphuric acid by a variety of combinations of double-conversion/absorption, single conversion/absorption, "low-bite" caesium catalyst, and tail-gas abatement. However, whatever the combination of techniques the following are the benchmarks for conversion efficiencies based on the feed of SO_2 to the "contact plant" (and the equivalent losses to air).

During start-ups, significantly higher release of SO_2 can be experienced but techniques should be employed to limit the releases to the levels in the last column below.

Sulphur conversion efficiencies	Normal operation		Start-up
	Conversion efficiency	Maximum loss	Maximum loss over first 5 hours
New plant	99.9 %	0.1 %	1.0 %
Existing plant	99.7 %	0.3 %	2.0 %

Note (e) - Volatile Organic Compounds (VOCs)

Where possible release of VOCs should be individually identified and, where practicable, monitored separately. The term 'volatile organic compounds' includes all organic compounds released to air in the gas phase. See also Appendix 3.

The VOC benchmark concentration levels apply where the following total mass release rates are exceeded, but releases below these mass emission rates may not be trivial for some substances so may still require controls and the setting of appropriate ELVs:

- Total Class A100 g/ hr
- Total Class B5 tonnes/ yr or 2 kg/ h, whichever is the lower (expressed as carbon)

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 displacement from a storage tank or process vessel. An approach based on limiting total mass released or mass per unit of production would be more appropriate.

3.2.2 Emissions to water associated with the use of BAT

Wastewater treatment systems can maximise the removal of metals using precipitation, sedimentation and possibly filtration. The reagents used for precipitation may be hydroxide, sulphide or a combination of both, depending on the mix of metals present. It is also practicable in many cases to re-use treated water.

Where automatic sampling systems are employed, limits may be defined such that:

- not more than 5% of samples shall exceed the benchmark value

Where spot samples are taken:

- no spot sample shall exceed the benchmark value by more than 50%

The range of substances that may be discharged to water from Inorganic processes is wide and depends entirely on the substance being produced, and the substances which are to be monitored should be selected according to the potential for their emission and subsequent impact. Refer to the process descriptions in **Section 2.1** for specific emissions.

Table 3.2: Benchmark levels for emissions to water

Substance	Level (mg/l) Notes (a) and (b)
Total hydrocarbon oil content (IR method)	1 - 3
Biological oxygen demand (BOD) (5 day ATU at 20 °C)	20 - 30
Chemical oxygen demand (COD) (2 hour)	30 - 125
Total nitrogen (as N)	10 - 15
Ammoniacal nitrogen (as N)	1 - 5
Suspended solids (dried at 105 °C)	20 - 30
Halogenated Organic Compounds (AOX)	1
Mercury	0.005
Cadmium	0.01
Copper, chromium, nickel and lead (each)	0.5
Zinc and tin (each)	2

Note (a)

- The levels given here are ranges achievable after effluent treatment and are not release limits. They are given on the basis of flow-weighted monthly averages.

- For pollutants resistant to biodegradation, achievement of the levels will require isolation at source and separate specialised treatment.
- On-site effluent treatment is generally preferred for installations in the sector but where discharge to sewer is proposed, it should be demonstrated that this option represents BAT - taking into account the substances released and their separability and degradability, the type of sewage treatment available, the security of the sewage treatment system (e.g. with regard to storm overflow), and the relative performance of that sewage treatment compared to the site-dedicated option. (Note: Compliance with trade effluent limits imposed by the sewage undertaker does not guarantee compliance with BAT.)

Note (b)

Some of the substances noted above (and others not noted above) will be included in List I or in List II of substances to which legislation stemming from the Dangerous Substances Directive applies. Individual ELVs set in accordance with the requirements of the DS Directive may be significantly lower than the benchmark values associated with BAT.

3.2.3 Standards and obligations

In addition to meeting the requirements of BAT, there are other national and international standards and obligations that must either be safeguarded through the IPPC Permit or, at least, taken into account in setting Permit conditions. This is particularly the case for any EC-based EQSs.

EC-based EQ standards

IPPC: A Practical Guide explains how these should be taken into account and contains an annex listing the relevant standards. (See **Appendix 2** for equivalent legislation in Scotland and Northern Ireland). They can be summarised as follows:

Air quality

- Statutory Instrument 2000 No.928, Air Quality (England) Regulations 2000 gives air quality objectives to be achieved by:
  - 2005 for nitrogen dioxide
  - 2004 for SO2 and PM10
  - 2003 for CO, 1,3-butadiene and benzene
  - in two stages for lead by 2004 and 2008 respectively
- Statutory Instrument 2002 No. 3043 The Air Quality (England) (Amendment) Regulations 2002, which sets a tighter objective for CO and a longer-term objective for benzene to be achieved by 2010.

Water quality

- Directive 76/464/EEC on Pollution Caused by Dangerous Substances Discharged to Water contains two lists of substances. List I relates to the most dangerous, and standards are set out in various daughter Directives. List II substances must also be controlled. Annual mean concentration limits for receiving waters for List I substances can be found in SI 1989/2286 and SI 1992/337 the Surface Water (Dangerous Substances Classification) Regulations. Values for List II substances are contained in SI 1997/2560 and SI 1998/389. Daughter Directives cover EQS values for mercury, cadmium, hexachlorocyclohexane, DDT, carbon tetrachloride, pentachlorophenol, aldrin, dieldrin, endrin, isodrin, hexachlorobenzene, hexachlorobutadiene, chloroform,1,2-dichloroethane, trichloroethane, perchloroethane and trichlorobenzene.

- Other waters with specific uses have water quality concentration limits for certain substances. These are covered by the following Regulations:
  - – SI 1991/1597 Bathing Waters (Classification) Regulations
  - – SI 1992/1331 and Direction 1997 Surface Waters (Fishlife) (Classification) Regulations
  - – SI 1997/1332 Surface Waters (Shellfish) (Classification) Regulations
  - – SI 1996/3001 The Surface Waters (Abstraction and Drinking Water) (Classification) Regulations

Other standards and obligations

Those most frequently applicable to most sectors are:

- Hazardous Waste Incineration Directive
- Waste Incineration Directive.
- Solvent Emissions Directive.
- Large Combustion Plant Directive.
- Reducing Emissions of VOCs and Levels of Ground Level Ozone: a UK Strategy (published by the Department of the Environment in October 1993. It sets out how the Government expects to meet its obligations under the UNECE VOCs Protocol to reduce its emissions by 30% (based on 1988 levels) by 1999, including the reductions projected for the major industrial sectors).
- Water Quality Objectives – assigned water quality objectives to inland rivers and water courses (ref. Surface (Rivers Ecosystem) Classification).
- The UNECE convention on long-range transboundary air pollution (negotiations are now underway which could lead to a requirement further to reduce emissions of NO_x and VOCs. A requirement to further reduce SO_2 emissions from all sources has been agreed. The second Sulphur protocol (Oslo, 1994) obliges the UK to reduce SO_2 emissions by 80% (based on 1980 levels) by 2010).
- The Montreal Protocol.
- The Habitats Directive (see **Section 4.3**).
- Sulphur Content of Certain Liquid Fuels Directive 1999/32/EC (from 1 January 2003, the sulphur content of heavy fuel oil must not exceed 1% except when it is burnt in plants fitted with SO_2 abatement equipment. Sulphur levels in gas oil must not exceed 0.2% from 1 July 2000, and 0.1% from the start of 2008.)

3.2.4 Units for benchmarks and setting limits in permits

Releases can be expressed in terms of:

- **“concentration”** (for example mg/l or mg/m3), which is a useful day-to-day measure of the effectiveness of any abatement plant and is usually measurable and enforceable The total flow must be measured/controlled as well
- **“specific mass release”** (for example, kg/ product or input or other appropriate parameter), which is a measure of the overall environmental performance of the plant (including the abatement plant) compared with similar plants elsewhere
- **“absolute mass release”** (for example, kg/hr, t/yr), which relates directly to environmental impact

When endeavouring to reduce the environmental impact of an installation, its performance against each of these levels should be considered, as appropriate to the circumstances, in assessing where improvements can best be made.

When setting limits in Permits, the most appropriate measure will depend on the purpose of the limit. It may also be appropriate to use surrogate parameters, which reflect optimum environmental performance of plant as the routine measurement, supported by less frequent check-analyses on the final concentration. Examples of surrogate measures would be the continuous measurement of conductivity (after ion-exchange treatment) or total carbon (before a guard-column in activated carbon treatment) to indicate when regeneration or replacement is required.

The emission level figures given in this chapter are based on average figures, not on maximum, short-term peak values, which could be expected to be higher. The emission levels given are based on a typical averaging period of not less than 30 minutes and not greater than 24 hours.

3.2.5 Statistical basis for benchmarks and limits in permits

Conditions in Permits can be set with percentile, mean or median values over annual, monthly or daily periods, which reflect probable variation in performance. In addition, absolute maxima can be set.

Where there are known failure modes, which will occur even when applying BAT, limits in Permits may be specifically disapplied, but with commensurate requirements to notify the Regulator and to take specific remedial action.

For water: UK benchmarks or limits are most frequently 95 percentile concentrations or absolute concentrations, (with flow limited on a daily average or maximum basis).

For air: benchmarks or limits are most frequently expressed as daily averages or, typically 95 percent of hourly averages.

3.2.6 Reference conditions for releases to air

The reference conditions of substances in releases to air from point-sources are:

- temperature 0°C (273K)
- pressure 101.3 kPa
- no correction for water vapour or oxygen

To convert measured values to reference conditions, see the **Monitoring Guidance** for more information.

3.3 Environmental Performance Indicators

Benchmark values in this guidance are typically presented as concentrations (e.g. mg/l, mg/Nm^3). Concentrations are the traditional basis for setting emission limits in permits as they are good indicators of unit operation performance but they have limitations. Thus, for England and Wales, the Environment Agency is developing complementary “Environmental Performance Indicators” that could help to target regulatory effort on the most important environmental issues.

Environmental Performance Indicators involve using emission data to:

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

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

For Air:

Stratospheric Ozone Depletion,

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

Photochemical Ozone Creation,

Airborne Acidification.

For Water:

Acidification,

Oxygen Demand,.

Eutrophication.

For Waste:

Waste Hazard Score (from H1),

Waste Disposal Score (from H1).

For raw materials:

Water use (potable and non-potable).

For hazardous substances:

Environmental Health,

Human Health.

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

The choice of Environmental Performance Indicators is left to Operators but they should give consideration to the issues that are listed above. The H1 database tool is advocated as providing a simple solution.

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

4 Impact

4.1 Impact assessment

The Operator should assess that the emissions resulting from the proposals for the activities/installation will provide a high level of protection for the environment as a whole, in particular having regard to EQS etc, revisiting the techniques in Section 2 as necessary. The use of **IPPC Environmental Assessments for BAT**, and the **IPPC Environmental Assessments for BAT software tool**, and the other tools on the Application CD, will lead the Applicant through the process.

The depth to which the impact assessment should go should be discussed with the Regulator. For some low risk sites the requirements may be reduced.

Indicative BAT requirements for impact assessment (Sheet 1 of 2)
Provide an assessment of the potential significant environmental effects (including transboundary effects) of the foreseeable emissions.

1 Provide a description, including maps as appropriate, of the receiving environment to identify the receptors of pollution. The extent of the area may cover the local, national and international (for example, transboundary effects) environment as appropriate.

2 Identify important receptors, which may include: areas of human population including noise or odour-sensitive areas, flora and fauna (that is, Habitat Directive sites, special areas of conservation, Sites of Special Scientific Interest (SSSI or in Northern Ireland ASSI) or other sensitive areas), soil, water, that is groundwater (water below the surface of the ground in the saturation zone and in direct contact with the ground and subsoil) and watercourses (for example, ditches, streams, brooks, rivers), air, including the upper atmosphere, landscape, material assets and the cultural heritage.

3 Identify the pathways by which the receptors will be exposed (where not self-evident).

4 Carry out an assessment of the potential impact of the total emissions from the activities on these receptors. **IPPC Environmental Assessments for BAT** provides a systematic method for doing this and will also identify where modelling needs to be carried out, to air or water, to improve the understanding of the dispersion of the emissions. The assessment will include comparison (see **IPPC: A Practical Guide**) with:

- community EQS levels
- other statutory obligations
- non-statutory obligations
- environmental action levels (EALs) and the other environmental and regulatory parameters defined in **IPPC Environmental Assessments for BAT**

5 In particular it will be necessary to demonstrate that an appropriate assessment of vent and chimney heights has been made to ensure that there is adequate dispersion of the minimised emission(s) to avoid exceeding local ground-level pollution thresholds and limit national and transboundary pollution impacts, based on the most sensitive receptor, be it human health, soil or terrestrial ecosystems.

Indicative BAT requirements for impact assessment (Sheet 2 of 2)
Provide an assessment of the potential significant environmental effects (including trans-boundary effects) of the foreseeable emissions.

6 Where appropriate, the Operator should also recognise the chimney or vent as an emergency emission point and understand the likely behaviour. Process upsets or equipment failure giving rise to abnormally high emission levels over short periods should be assessed. Even if the Applicant can demonstrate a very low probability of occurrence, the height of the chimney or vent should nevertheless be set to avoid any significant risk to health. The impact of fugitive emissions can also be assessed in many cases.

7 Consider whether the responses to Sections 2 and 3 and this assessment adequately demonstrate that the necessary measures have been taken against pollution, in particular by the application of BAT, and that no significant pollution will be caused. Where there is uncertainty about this, the measures in Section 2 should be revisited as appropriate to make further improvements.

8 Where the same pollutants are being emitted by more than one permitted activity on the installation, the Operator should assess the impact both with and without the neighbouring emissions.

4.2 Waste Management Licensing Regulations

Indicative BAT requirements for waste management licensing regulations
Explain how the information provided in other parts of the application also demonstrates that the requirements of the relevant objectives of the Waste Management Licensing Regulations 1994 have been addressed, or provide additional information in this respect.

1 In relation to activities involving the disposal or recovery of waste, the Regulators are required to exercise their functions for the purpose of achieving the relevant objectives as set out in Schedule 4 of the Waste Management Licensing Regulations 1994. (For the equivalent Regulations in Scotland and Northern Ireland, see **Appendix 2**.)

2 The relevant objectives, contained in paragraph 4, Schedule 4 of the Waste Management Licensing Regulations 1994 (SI 1994/1056 as amended) are extensive, but will only require attention for activities that involve the recovery or disposal of waste. Paragraph 4 (1) is as follows:

- ensuring the waste is recovered or disposed of without endangering human health and without using process or methods which could harm the environment and in particular without:
  - risk to water, air, soil, plants or animals or
  - causing nuisance through noise or odours or
  - adversely affecting the countryside or places of special interest
- implementing, as far as material, any plan made under the plan-making provisions

3 The application of BAT is likely to already address risks to water, air, soil, plants or animals, odour nuisance and some aspects of effects on the countryside. It will, however, be necessary for the Operator briefly to consider each of these objectives individually and provide a comment on how they are being addressed by your proposals. It is also necessary to ensure that any places of special concern that could be affected, such as SSSIs, are identified and commented upon although, again, these may have been addressed in your assessment for BAT, in which case a cross-reference may suffice.

4 Operators should identify any development plans made by the local planning authority, including any waste local plan, and comment on the extent to which the proposals accord with the contents of any such plan (see **Section 2.6**).

4.3 The Habitats Regulations

Indicative BAT requirements for the habitats regulations
Provide an assessment of whether the installation is likely to have a significant effect on a European site in the UK and, if it is, provide an assessment of the implications of the installation for that site, for the purpose of the Conservation (Natural Habitats etc.) Regulations 1994 (SI 1994/2716)

1 An application for an IPPC Permit will be regarded as a new plan or project for the purposes of the Habitats Regulations (for the equivalent Regulations in Scotland and Northern Ireland see **Appendix 2**). Therefore, Operators should provide an initial assessment of whether the installation is likely to have a significant effect on any European site in the UK (either alone or in combination with other relevant plans or projects) and, if so, an initial assessment of the implications of the installation for any such site. The application of BAT is likely to have gone some way towards addressing the potential impact of the installation on European sites and putting into place techniques to avoid any significant effects. The Operator should provide a description of how the BAT assessment has specifically taken these matters into account, bearing in mind the conservation objectives of any such site.

2 European sites are defined in Regulation 10 of the Habitats Regulations to include Special Areas of Conservation (SACs); sites of community importance (sites that have been selected as candidate SACs by member states and adopted by the European Commission, but which are not yet formally classified); and Special Protection Areas (SPAs). It is also Government policy (set out in PPG 9 on nature conservation) that potential SPAs and candidate SACs should be considered to be European sites for the purposes of Regulation 10.

3 Information on the location of European sites and their conservation objectives is available from:

- English Nature (01733 455000), **www.english-nature.org.uk**
- Countryside Council for Wales (01248 385620), **www.ccw.gov.uk**
- Scottish Natural Heritage (0131 447 4784), **www.snh.org.uk**
- Joint Nature Conservation Committee (01733 866852), **www.jncc.gov.uk**
- Environment and Heritage Service, Northern Ireland (02890254754), **www.ehsni.gov.uk**

4 The Regulator will need to consider the Operator's initial assessment. If it concludes that the installation is likely to have a significant effect on a European site, then the Regulator will need to carry out an “appropriate assessment” of the implications of the installation in view of that site's conservation objectives. The Regulations impose a duty on the Regulator to carry out these assessments, so it cannot rely on the Operator's initial assessments. Therefore the Regulator must be provided with any relevant information upon which the Operator’s assessment is based.

5 Note that in many cases the impact of the Habitats Regulations will have been considered at the planning application stage, in which case the Regulator should be advised of the details.

References

For a full list of available Technical Guidance see Appendix A of the Guide for Applicants or visit the Environment Agency Website **http://www.environment-agency.gov.uk**. Many of the references below are being made available free of charge for viewing or download on the Website. The same information can also be accessed via the SEPA web site **http://www.sepa.org.uk**, or the NIEHS web site **www.ehsni.gov.uk**. Most titles will also be available in hard copy from The Stationery Office (TSO). Some existing titles are not yet available on the Website but can be obtained from TSO.

Ref 1 IPPC Reference Document on Best Available Techniques (BREFs) - European Commission **http://eippcb.jrc.es**. BREFS with content relevant to the Inorganic Chemicals sector include:

- *Chlor-Alkali industry,* (December 2001)
- *Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilizers,* (2nd Draft, March 2004)
- *Large Volume Organic Chemical Industry,* (February 2003)
- *Speciality Organic Chemicals,* (Draft March 2004)
- *Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector,* (February 2003)
- *Emissions from Storage,* (2nd draft, July 2003)
- *Industrial Cooling Systems,* (December 2001)
- *Cement and Lime Mnufacturing Industries,* (December 2001)
- *General Principles of Monitoring,* (July 2003)
- *Economics and Cross-media Effects,* (2nd draft, September 2003)
- *Mineral Oil and Gas Refineries,* (February 2003)
- *Waste Incineration,* (2nd draft, March 2004)
- *Waste Treatments Industries,* (2nd draft, January 2004)
- *Large Combustion Plant,* (2nd draft, March 2003)

Ref 2 *The Pollution Prevention and Control Act (1999)* (**www.hmso.gov.uk**).

Ref 3 *The Pollution Prevention and Control Regulations* (SI 2000 No. 1973) (**www.hmso.gov.uk**).

Ref 4 *IPPC: A Practical Guide; Edition 3, 2004* (for England and Wales) (or its equivalents in Scotland and Northern Ireland) **www.defra.gov.uk**

Ref 5 Guidance for applicants

- *IPPC Part A(1) Installations: Guide for Applicants (England and Wales)* **www.environment-agency.gov.uk**
- *PPC Part A Installations: Guide for Applicants (Scotland)* (Guidance for SEPA staff on land and groundwater considerations) **www.sepa.org.uk**
- *Integrated Pollution Prevention and Control (IPPC),Guide for Applicants (Northern Ireland)* **www.ehsni.gov.uk**
- *IPPC Regulatory Guidance Series No.5 - Interpretation of "Installation" in the PPC Regulations* **www.environment-agency.gov.uk**

Ref 6 Assessment methodologies:

- *Environmental Assessment and Appraisal of BAT (Horizontal Guidance Note IPPC H1 - Issue 2, November 2002)* **www.environment-agency.gov.uk**

Ref 7 Waste minimisation and raw materials efficiency references

- *Environment Agency's web page*. Waste minimisation information accessible via: **www.environment-agency.gov.uk/subjects/waste/131528**
- *Waste Minimisation – an environmental good practice guide for industry* (helps industry to minimise waste and achieve national environmental goals). Available free to companies who intend to undertake a waste reduction programme (tel: 0345 33 77 00)
- *Profiting from Pollution Prevention – 3Es methodology* (emissions, efficiency, economics). Video and A4 guide aimed at process industries. Available from Environment Agency, North East region, Regional PIR (tel: 0113 244 0191)
- *Envirowise*. A joint DTI/DEFRA programme, with over 200 separate case studies, good practice guides, leaflets, flyers, software tools, environmental benchmarking, etc covering 12 industry sectors, packaging, solvent use and the generic areas of waste minimisation, reduced water usage and effluent flow, and cleaner technology. Envirowise is accessible via a free and confidential helpline (tel: 0800 585 794) or via the web site **www.envirowise.gov.uk**

- *Waste Minimisation Interactive Tools (WIMIT)*. Produced by Envirowise in association with the Environment Agency and the BOC Foundation (a software tool designed for small- and medium-businesses). Available free from the Envirowise Helpline (tel: 0800 585 794)
- *Waste Management Information Bureau*. The UK's national referral centre for help on the full range of waste management issues. It produces a database called Waste Info, which is available for on-line searching and on CD-ROM. Short enquiries are free. (tel: 01235 463 162)
- *Waste Minimisation - A Practical Guide*, Institution of Chemical Engineers,1995, plus Training Package E07. Basic course which contains guide, video, slides, OHPs etc. (tel: 01788 578 214)

Ref 8 Water efficiency references:

- *Envirowise* (see Ref 7) More than 50 case studies, good practice guides, software tools, environmental benchmarking, etc on the subject of reduced water usage and effluent discharges.
- *Optimum use of water for industry and agriculture dependent on direct abstraction: Best practice manual*. R&D technical report W157, Environment Agency (1998), WRc Dissemination Centre, Swindon (tel: 01793 865 012)

Ref 9 Releases to air references:

- *Waste Water and Waste Gas Treatment BREF,* (see Ref 1)
- *Guidance on effective flaring in the gas, petroleum and associated industries,* HMIP Technical Guidance Note (Abatement) A1, 1993, ISBN 0-11-752916-8 **www.tso.co.uk/bookshop**
- *Pollution abatement technology for the reduction of solvent vapour emissions,* HMIP Technical Guidance Note (Abatement) A2, 1994, ISBN 0-11-752925-7 **www.tso.co.uk/bookshop**
- *Pollution abatement technology for particulate and trace gas removal,* HMIP Technical Guidance Note (Abatement) A3, 1994, ISBN 0-11-752983-4 **www.tso.co.uk/bookshop**
- *BIO-WISE - profiting through industrial biotechnology,* A DTI programme of Case Studies, demonstrator programmes and guides to the use of biotechnology to improve the environmental performance of sectors such as Chemicals and Engineering - including reduction in emissions to water and to air. Free advice and information is availble from the BIO-WISE web site **www.dti.gov.uk/biowise** and Helpline 0800 432 100
- *Envirowise,* (see Ref 7) A variety of case studies, good practice guides, software tools, environmental benchmarking, etc, on the subject of reducing emissions to air
- *Guidelines on Discharge Stack Heights for Polluting Emissions,* HMIP Technical Guidance Note (Dispersion) D1 (see Ref 17)

Ref 10 Releases to water references

- *Waste Water and Waste Gas Treatment BREF* (see Ref 1)
- *Effluent Treatment Techniques,* Environment Agency Technical Guidance Note (Abatement) A4, 1997, ISBN 0-11-310127-9 **www.tso.co.uk/bookshop**
- *Envirowise* (see Ref 7) More than 50 cases studies, good practice guides, software tools, environmental benchmarking, etc, on the subject of reducing water pollution and usage.
- *PPG 02 - Above-ground oil storage tanks,* Environment Agency Pollution Prevention Guidance Note. Provides information on tanks and bunding which has general relevance beyond just oil **www.environment-agency.gov.uk**
- *PPG 03 - The use and design of oil separators in surface water drainage systems,* Environment Agency Pollution Prevention Guidance Note **www.environment-agency.gov.uk**
- *PPG 18 - Managing Fire-water and major spillages,* Environment Agency Pollution Prevention Guidance Note **www.environment-agency.gov.uk**
- *PPG 26 - Storage and handling of intermediate bulk containers,* Environment Agency Pollution Prevention Guidance Note **www.environment-agency.gov.uk**
- *Construction of bunds for oil storage tanks*, Mason, P. A, Amiss, H. J, Sangarapillai, G. Rose, Construction Industry Research and Information Association (CIRIA), Report 163, 1997, CIRIA, 6 Storey’s Gate, Westminster, London SW1P 3AU. Abbreviated versions are also available for masonry and concrete bunds. **www.ciria.org.uk** or **www.environment-agency.gov.uk**

Ref 11 Waste management references

- *Investigation of the criteria for, and guidance on, the landspreading of industrial wastes* – final report to the DEFRA, the Environment Agency and MAFF, May 1998

Ref 12 Energy references

- *(Interim) Energy Efficiency Guidance,*(available as draft Horizontal Guidance Note IPPC H2) (**www.environment-agency.gov.uk)**

Ref 13 COMAH guides

- *A Guide to the Control of Major Accident Hazards Regulations 1999*, Health and Safety Executive (HSE) Books L111, 1999, ISBN 0 07176 1604 5

• *Preparing Safety Reports: Control of Major Accident Hazards Regulations 1999*, HSE Books HS(G)190, 1999

• *Emergency Planning for Major Accidents: Control of Major Accident Hazards Regulations 1999*, HSE Books HS(G)191, 1999

• *Guidance on the Environmental Risk Assessment Aspects of COMAH Safety Reports*, Environment Agency, 1999 (**EA website**)

• *Guidance on the Interpretation of Major Accidents to the Environment for the Purposes of the COMAH Regulations*, DEFRA, 1999, ISBN 753501 X, available from the Stationery Office

Ref 14 Monitoring Guidance

= *MCERTS approved equipment* link via **www.mcerts.net**

= *Technical Guidance Note M1 - Sampling requirements for monitoring stack emissions to air from industrial installations,* Version 2, Environment Agency, 2002. **www.environment-agency.gov.uk**

= *Technical Guidance Note M2 - Monitoring of stack emissions to air,* Version 2, Environment Agency, 2003. **www.environment-agency.gov.uk**

= *Technical Guidance Note M18 - Monitoring of discharges to water,* Version 1, Environment Agency,, 2004. **www.environment-agency.gov.uk**

• *Direct Toxicity Assessment for Effluent Control* Technical Guidance (2000), UKWIR 00/TX/02/07

Ref 15 Noise references:

= *H3 Horizontal Guidance for Noise Part 1* Regulation and Permitting

• *H3 Horizontal Guidance for Noise Part 2* Assessment and Control

Ref 16 Closure references

Ref 17 *Working at Construction and Demolition-sites* (PPG 6) (**EA website**)

Ref 18 Air Dispersion

• *Guidelines on Discharge Stack Heights for Polluting Emissions,* HMIP Technical Guidance Note (Dispersion) D1, 1993, ISBN 0-11-752794-7 **www.tso.co.uk/bookshop**; (or **www.environment-agency.gov.uk** for summary only)

Ref 19 Fire Fighting

• *BS 5908: Code of Practice for Fire Precautions in the Chemical and Allied Industries*

• *PPG 18 - Managing Fire-water and major spillages,* Environment Agency Pollution Prevention Guidance Note (see Ref 10)

Ref 20 Volatile Organic Compounds

• *The Categorisation of Volatile Organic Compounds,*1995 HMIP Research Report No DOE/HMIP/RR/95/009 (**www.environment-agency.gov.uk**)

Ref 21 Environment Agency Technical Guidance for the previous (IPC) regulatory regime

• *Inorganic Acids and Halogens,* IPC S2 4.03, Environment Agency, 1999, ISBN 0-11-310141-4 **www.tso.co.uk/bookshop** or **www.environment-agency.gov.uk**

• *Inorganic Chemicals,* IPC S2 4.04, Environment Agency, 1999, ISBN 0-11-310140-6 **www.tso.co.uk/bookshop** or **www.environment-agency.gov.uk**

• *Combustion Processes: Large Boilers and Furnaces 50 MW(th) and over,* IPC S2 1.01, HMSO, ISBN 0-11-310120-1 **www.tso.co.uk/bookshop** or **www.environment-agency.gov.uk**

Ref 22 Odour references:

• *H4 Horizontal Guidance for Odour Part 1* - Regulation and Permitting - **www.environment-agency.gov.uk**

• *H4 Horizontal Guidance for Odour Part 2* - Assessment and Control - **www.environment-agency.gov.uk**

Ref 23 Relevant Environment Agency sectoral IPPC Technical Guidance Notes

• *Guidance for the Large Volume Organic Chemicals Sector,* IPPC S4.01 - **www.environment-agency.gov.uk**

• *Guidance for the Speciality Organic Chemicals Sector,* IPPC S4.02 - **www.environment-agency.gov.uk**

• *Guidance for the Cement and Lime Sector,* IPPC S3.01 - **www.environment-agency.gov.uk**

• *Guidance for the incineration of Waste and Fuel manufactured from or including waste,* IPPC S5.01 - **www.environment-agency.gov.uk**

Ref 24 Titanium Dioxide Directive

• *EC Directive on Procedures for Harmonising the Programmes for the Reduction and Eventual Elimination of Pollution caused by Waste from the Titanium Dioxide Industry, 92/112/EEC*

Ref 25 Storage of Ammonia

• *Storage of Anhydrous Ammonia under Pressure in the UK,* HS(G) 30, Health and Safety Executive, 1986

Ref 26 Handling of Hydrogen Cyanide

- *Code of Practice for Chemicals with Major Hazards: The safe design, construction and use of plants producing or consuming hydrogen cyanide,* BASF plc, Hampshire Chemicals Ltd, ICI plc, Nov 1993

Abbreviations

BAT	Best Available Techniques – see IPPC A Practical Guide or the Regulations for further definition
BAT Criteria	The criteria to be taken into account when assessing BAT, given in Schedule 2 of the PPC Regulations
BOD	Biochemical Oxygen Demand
BREF	BAT Reference Document
CEM	Continuous Emissions Monitoring
CHP	Combined heat and power plant
COD	Chemical Oxygen Demand
ELV	Emission Limit Value
EMS	Environmental Management System
EQS	Environmental Quality Standard
ETP	Effluent treatment plant
FOG	Fat Oil Grease
ITEQ	International Toxicity Equivalents
MCERTS	Monitoring Certification Scheme
NIEHS	Northern Ireland Environment and Heritage Service
SAC	Special Areas of Conservation
SECp	Specific Energy consumption
SEPA	Scottish Environment Protection Agency
SPA	Special Protection Area
TSS	Suspended solids
TOC	Total Organic Carbon
VOC	Volatile organic compounds

Appendix 1: Some common monitoring and sampling methods

The Agency's Technical Guidance Notes (Monitoring) M1, Sampling Requirements for Monitoring Stack Emissions to Air from Industrial Installations, and M2, Monitoring of Stack Emissions to Air, are available via the "Search Site" facility on the Agency's web page, http://www.environment-agency.gov.uk/, entering M1 or M2 as the keyword. These documents provide key references as regards more detailed insight into different approaches to monitoring stack emissions, sampling strategies and choice of technique, method, and equipment. Relative advantages and disadvantages of continuous versus periodic measurements are summarised in Part 2 of M2. Situations where continuous monitoring (continuous emissions monitoring systems - CEMs) may be more appropriate are discussed further in Section 5 of this note. Manual sampling and analysis methods are used to meet periodic or intermittent regulatory monitoring requirements and in some cases for validation and calibration of CEMs.

Table 4.1: Measurement methods for common substances to water

Determinand	Method	Detection limit Uncertainty	Valid for range mg/l	Standard
Suspended solids	Filtration through glass fibre filters	1 mg/l 20%	10-40	ISO 11929:1997, EN872 - Determination of suspended solids
COD	Oxidation with dichromate	12 mg/l 20%	50-400	ISO 6060: 1989, Water Quality - Determination of chemical oxygen demand
BOD5	Seeding with micro-organisms and measurement of oxygen content	2 mg/l 20%	5-30	ISO 5815: 1989, Water Quality Determination of BOD after 5 days, dilution and seeding method EN 1899 (BOD 2 Parts)
AOX	Adsorption on activated carbon and combustion	-- 20%	0.4 - 1.0	ISO 9562: 1998, EN1485 - Determination of adsorbable organically bound halogens.
Tot P				BS 6068: Section 2.28 1997, Determination of phosphorus –ammonium molybdate spectrometric method
Tot N				BS 6068: Section 2.62 1998, Determination of nitrogen Part 1 Method using oxidative digestion with peroxydisulphate, BS EN ISO 11905
pH				SCA The measurement of electric conductivity and the determination of pH, ISBN 0117514284
Turbidity				SCA Colour and turbidity of waters 1981, ISBN 0117519553 EN 27027:1999
Flow rate	Mechanical ultrasonic or electromagnetic gauges			SCA Estimation of Flow and Load, ISBN 011752364X
Temperature				
TOC				SCA The Instrumental Determination of Total Organic Carbon and Related Determinants 1995, ISNB 0117529796 EN 1484:1997
Fatty acids				Determination of Volatile Fatty Acids in Sewage Sludge 1979, ISBN 0117514624
Metals				BS 6068: Section 2.60 1998, Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy
Chlorine				BS6068: Section 2.27 1990, Method for the determination of total chlorine: iodometric titration method

Table 4.1: Measurement methods for common substances to water

Determinand	Method	Detection limit Uncertainty	Valid for range mg/l	Standard
Chloroform Bromoform				BS 6068: Section 2.58, Determination of highly volatile halogenetaed hydrocarbons – Gas chromatographic methods
Dispersants Surfactants Anionic Cationic Non-ionic				SCA Analysis of Surfactants in Waters, Wastewaters and Sludges, ISBN 01176058 EN 903:1993 (Used for anionic surfactants)
Pentachloro-Phenol				BS5666 Part 6 1983, Wood preservative and treated timber quantitative analysis of wood preservatives containing pentachlorophenol EN 12673:1997 (used for chlorophenol and polychlorinated phenols)
Formaldehyde				SCA The determination of formaldehyde, other volatile aldehydes and alcohols in water
Phosphates and nitrates				BS 6068: Section 2.53 1997, Determination of dissolved ions by liquid chromatography
Sulphites and sulphates				BS 6068: Section 2.53 1997, Determination of dissolved ions by liquid chromatography
Ammonia				BS 6068: Section 2.11 1987, Method for the determination of ammonium: automated spectrometric method
Grease and oils	IR absorption	0.06 mg/kg		SCA The determination of hydrocarbon oils in waters by solvent extraction IR absorption and gravimetry, ISBN 011751 7283

Table 4.2: Measurement methods for air emissions

Determinand	Method	Av'ging time Detection limit Uncertainty	Compliance criterion	Standard
Formaldehyde	Impingement In 2,4 dinitro-phenyl-Hydrazine HPLC	1 hour 1 mg/m^3 30%	Average of 3 consecutive samples below specified limit	US EPA Method 316 Method specific to formaldehyde.
Ammonia	FTIR or Ion Chromatography	1 hour 0.5mg/m^3 25%		US EPA Method 320 for extractive instruments. US EPA Method 26 for wet chemistry.
VOCs	Speciated - Adsorption Thermal Desorption GCMS	1 hour 0.1 mg/m^3 30%		BS EN 1076:1997 Workplace atmospheres. Pumped sorbent tubes for the determination of gases and vapours. Requirements and test methods.
	Total Organic Carbon	1 hour 0.4 mg/m^3 calculated	Continuous or spot check	BS EN 12619:1999. Determination of the mass concentration of total gaseous organic carbon at low concentrations in flue gases – continuous flame ionisation method.3
Chloroform	Absorption on activated carbon solvent extraction. GC analysis	1 hour 1 mg/m^3 20%	Average of 3 consecutive samples below specified limit	MDHS 28 Chlorinated hydrocarbon solvent vapours in air (modified)
Oxides of Sulphur	UV fluorescence Automatic analyser	1 hour 1 ppm 10%	95% of hourly averages over a year below specified limit	BS6069 Section 4.4 :1993 (ISO 7935) Stationary source emissions-determination of mass concentrations of sulphur dioxide4.

Table 4.2: Measurement methods for air emissions

Determinand	Method	Av'ging time Detection limit Uncertainty	Compliance criterion	Standard
	Wet sampling train Ion chromatography	1 hour 1 mg/m^3 25%	Average of 3 consecutive samples below specified limit	BS6069 Section 4.1:1998 (ISO 7934) Method for the determination of the mass concentration of sulphur dioxide-hydrogen peroxide/barium perchlorate method
Hydrogen Chloride	Wet sampling 3 analytical methods	30 minute minimum 0.2 mg/m^3 calculated	One test	BS EN 1911:Parts 1-3:1998 Manual method of determination of HCl
Particulate matter	Extractive – sample train	3 minutes per point 5 mg/m^3 10%	One test	BS EN 13284-1:2002 Determination of low range mass concentration of dust — Part 1: Manual gravimetric method.
	Continuous – Automatic analyser	Continuous N/A 10%	Continuous	BS ISO 10155:1995Automated Monitoring of mass concentrations of particles – performance characteristics, test methods and specifications.
PCDD/F	Extractive – Sample train GC/MS	4 hour minimum 8 hour maximum 0.1 ng I-TEQ/m^3 calculated		BS EN 1948:1997 determination of the mass concentration of PCDD/F

Measurement uncertainty is defined as total expanded uncertainty at 95% confidence limit calculated in accordance with the Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9, 1st Ed., Geneva, Switzerland, ISO 1993.

See also **Monitoring Guidance**

Appendix 2: Equivalent legislation in Wales, Scotland & Northern Ireland

The legislation referred to in the text is that for England. The following are the equivalents for Scotland, Wales and Northern Ireland.

Table 4.3: Equivalent legislation

England	Wales	Scotland	Northern Ireland
PPC Regulations (England and Wales) 2000, SI 2000 No.273 (as amended)	As England	PPC (Scotland) Regulations 2000, SSI 2000 No.323 (as amended)	PPC (NI) Regulations 2003, SR 2003 No.323
SI:1994 1056: Waste Management Licensing Regulations	As England	As England	To be prepared
The Water Resources Act 1991	As England	COPA 1974 (S30A-30E equiv to Part III WRA91): Natural Heritage (Scotland) Act 1991 (Part II equiv to Part I WRA91)	The Water (NI) Order 1999
SI 1989 No.317: Clean Air, The Air Quality Standards Regulations 1989	As England	As England	SR 1990 No.145: The Air Quality Standards Regulations (Northern Ireland) 1990
SI 1995 No. 3146: The Air Quality Standards (Amendments) Regulations 1995			SR1996 No.23: The Air Quality Standards (Amendments) Regulations (Northern Ireland) 1996
SI 2002 No. 3043 The Air Quality (England) (Amendment) Regulations 2002	SI 2002 No. 3182 (W.298) The Air Quality (Amendment) (Wales) Regulations 2002	SSI 2002 No. 297 The Air Quality (Scotland) Amendment Regulations 2002	
SI 2000 No.928: The Air Quality (England) Regulations 2000	SI 2000 No.1940 (W.138): The Air Quality (Wales) Regulations 2000	SSI 2000/97: The Air Quality (Scotland) Regulations	No NI equivalent
SI 2002 No. 3117 The Air Quality Limit Values (Amendment) Regulations 2002	SI 2002 No. 3183 (W.299) The Air Quality Limit Values (Wales) Regulations 2002	SSI 2002 No. 566 The Air Quality Limit Values (Scotland) Amendment Regulations 2002	
SI 2001 No.2315: The Air Quality Limit Values Regulations 2001	SI 2001 No.2683 (W.224): The Air Quality Limit Values (Wales) Regulations 2001	SSI 2001 No.224: The Air Quality Limit Values (Scotland) Regulations 2001	SI 2002 No.94: The Air Quality Limit Values (Northern Ireland) Regulations 2002
SI 1989 No 2286 and 1998 No 389: The Surface Water (Dangerous Substances Classification) Regulations. (Values for List II substances are contained in SI 1997/2560 and SI 1998/389)	As England	SI 1990/126: Surface Water (Dangerous Substances) (Classification) (Scotland) Regulations	Surface Waters (Dangerous Substances) (Classification) Regulations 1998. Statutory Rules of Northern Ireland 1998 No 397
SI 1991 No.1597: Bathing Waters (Classification) Regulations 1991	As England	SI 1991 No.1609: Bathing Waters (Classification) (Scotland) Regulations 1991	The Quality of Bathing Water Regulations (NI) 1993

Table 4.3: Equivalent legislation

England	Wales	Scotland	Northern Ireland
SI 1997 No.1331: The Surface Waters (Fishlife) (Classification) Regulations 1997	As England	SI 1997 No.2471 (S.163): The Surface Waters (Fishlife) (Classification) (Scotland) Regulations 1997	The Surface Water (Fishlife) (Classification) Regulations (NI) 1997
SI 1997 No.1332: The Surface Waters (Shellfish) (Classification) Regulations 1997	As England	SI 1997 No.2470 (S.162): The Surface Waters (Shellfish) (Classification) (Scotland) Regulations 1997	The Surface Water (Shellfish) (Classification) Regulations (NI) 1997
SI 1994 No.2716: The Conservation (Natural Habitats, etc) Regulations	As England	As England	Conservation (Natural Habitats etc) Regulations (Northern Ireland) 1995
SI 1999 No.743: Control of Major Accident Hazards Regulations (COMAH) 1999	As England	As England	SR 2000 No.93: Control of Major Accident Hazards Regulations (Northern Ireland) 2000
SI 1998 No.2746: The Groundwater Regulations 1998	As England	As England	SR 1998 No.401. The Groundwater Regulations (Northern IrelandI) 1998

Appendix 3: Volatile Organic Compounds

Introduction

Volatile organic compounds (VOCs) are of serious environmental concern because of the harmful or offensive properties that they exhibit in varying degrees. These include:

- direct toxicity to human health and other eco-systems
- contribution to photochemical ozone creation at ground level with consequent harmful effects
- destruction of stratospheric ozone
- contribution to global climate change; and
- sensory effects such as malodour

The harmfulness of VOCs varies greatly, not only because the individual and combined significance of these properties exhibits wide variation between substances, but also because it is dependent on the presence of the substance in the environment. This is related to mass release rate and subsequent dispersion and to the environmental persistence and fate of the substance under prevailing conditions.

Categorisation

In order to assess BAT for processes that release VOCs, it is necessary to categorise VOCs according to their harmfulness.

Substances such as benzene, vinyl chloride and 1,2- dichloroethane pose serious health risks to humans and are regarded as highly harmful. These are given individual, very low achievable levels of emission in guidance.

Some other VOCs carry a lesser but still significant health risk or may contribute substantially to photochemical ozone creation or stratospheric ozone destruction or global warming. These are regarded as of medium harmfulness and are allocated to Class A. They will include the substances listed in the Montreal Protocol, the phase-out of which is covered by EC Regulations 594/91, 3952/92, 2047/93 and 3093/94.

The remaining majority of VOCs are of low harmfulness but are also substances whose release should be prevented or minimised. These are allocated to Class B.

Odorous VOCs may be offensive at extremely low concentrations and this property may indicate the need for very tight control of a substance that would otherwise be categorised as of low harmfulness.

The research report "The Categorisation of Volatile Organic Compounds" (DOE/HMIP/RR/95/009) provides a method of categorisation, information on the properties of some 500 VOCs and a summary table of resulting categorisations.

In seeking to categorise a VOC, first search the summary table of categorisations. If the VOC is not included, the method and decision tree given in the research report should be used to arrive at a conclusion supported as well as possible by information from established sources. These include the Registry of Toxic Effects of Chemicals, the "CHIP" list, the Montreal Protocol and Sax' Dangerous Properties of Industrial Materials.

Knowledge of the harmful effects of VOCs is developing and there may be occasional differences of experts' opinions on the precise interpretation of information. In these few instances, it will be prudent to adopt the more cautious view.

Achievable Benchmark Levels

The levels of emission that can be achieved are dependent on factors that include the process itself, the VOC concerned and the abatement method used.

Where possible, process- and substance-specific achievable levels of release are given in Table 3.1 of this Note. However, in the absence of sufficient information or where it is agreed that an assessment is not possible, the following guidelines may be used to provide a practical approach to setting limits.

- The benchmark release concentrations given below should be aimed for where the following mass release limits are exceeded:

  Total Class A - 100 g/h
  Total Class B (expressed as carbon) - 2 kg/h

  - but emissions below these mass emission levels may not be trivial, and so may still require controls and the setting of appropriate release limits.
- Highly harmful VOCs pose major human health risks and have individual guidance levels given in Table 3.1 of this Note.
- For Class A compounds, BATabatement techniques should achieve a benchmark release level of 20 mg/m^3 for continuous emissions.
- Some VOCs cause significant malodour problems even at very low concentrations after dispersion, and limits lower than Class A compounds may be required.
- Class B compounds are those of low environmental harmfulness such as acetone and toluene and the Class B benchmark level has been set at 75 mg/m^3 (expressed as carbon) based on abatement techniques involving adsorption with activated carbon.
- For mixed streams the release level may be calculated by summing the class levels multiplied by their respective mass fractions.
- The use of a release concentration limit is not normally appropriate in the case of a release from an air-deficient saturated vapour space such as storage tanks for solvents or process vessels. An approach based on limiting total mass released or mass per unit of production is likely to be more effective.
- In some processes, the VOCs released to air may well consist of partial oxidation products rather than defined compounds that can be classified as above. In such cases an approach based on a TOC release concentration is likely to be more appropriate.

Appendix 4: Groundwater Regulations 1998. Schedule of listed substances and recommendations for List I

List I

1.-(1) Subject to the sub paragraph below, a substance is in List I if it belongs to one of the following families or groups of substances:

- (a) organohalogen compounds and substances that may form such compounds in the aquatic environment
- (b) organotin compounds
- (c) substances that possess carcinogenic, mutagenic or teratogenic properties in or via the aquatic environment (including substances that have those properties that would otherwise be in List II)
- (d) mercury and its compounds
- (e) cadmium and its compounds
- (f) mineral oils and hydrocarbons
- (g) cyanides.

1.-(2) A substance is not in List I if it has been determined by the Regulator to be inappropriate to List I on the basis of a low risk of toxicity, persistence and bioaccumulation.

List II

2.-(1) A substance is in List II if it could have a harmful effect on groundwater and it belongs to one of these families or groups of substances:

- (a) the following metalloids and metals and their compounds:
    - zinc
    - barium
    - chromium
    - uranium
    - arsenic
    - thallium
    - titanium
    - tin
    - nickel
    - boron
    - selenium
    - cobalt
    - molybdenum
    - silver
    - copper
    - beryllium
    - lead
    - vanadium
    - antimony
    - tellurium
- (b) biocides and their derivatives not appearing in List I
- (c) substances that have a harmful effect on the taste or odour of groundwater, and compounds liable to cause the formation of such substances in such water and to render it unfit for human consumption
- (d) toxic or persistent organic compounds of silicon, and substances that may cause the formation of such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances
- (e) inorganic compounds of phosphorus and elemental phosphorus
- (f) fluorides
- (g) ammonia and nitrates.

2.-(2) A substance is also in List 2 if:

- (a) it belongs to one of the families or groups of substances set out in paragraph 1(1) above

(b) it has been determined by the Regulator to be inappropriate to List I under paragraph 1(2); and

(c) it has been determined by the Regulator to be in inappropriate to List II having regard to toxicity, persistence and bioaccumulation.

3.-(1) The Secretary of State or Scottish Ministers may review any decision of the Regulator in relation to the exercise of its powers under the paragraphs above.

3.-(2) The Secretary of State or Scottish Minister shall notify the Regulator of his decision following a review under List 1 sub paragraph 1 above and it shall be the duty of the Regulator to give effect to that decision.

4.- The Regulator shall from time to time publish a summary of the effect of its determinations under this Schedule in such manner as it considers appropriate and shall make copies of any such summary available to the public free of charge.

List of substances recommended to be confirmed as List I

- as recommended by the Joint Agency Groundwater Directive Advisory Group.

Aldrin
Atrazine
Azinphos-ethyl
Bromoxynil (as Bromoxynil-phenol)
Bromoxynil octanoate
Cadmium
2-Chloroaniline
Chlorobenzene
Chlordane
Chloro-2,4-dinitrobenzene
Chlorfenvinphos
4-Chloro-3-methylphenol
Chloro-2-nitrobenzene
Chloro-3-nitrobenzene
Chloro-4-nitrobenzene
2-Chlorophenol
Chlorothalonil
2-Chlorotoluene
a-Chlorotoluene
Chlorpyrifos
Coumaphos
Cypermethrin
DDT
Demeton
Diazinon
Dibutyl bis(oxylauroyl)tin
Dichlofluanid
Diuron
Endosulfan
Fenitrothion
Fenthion
Heptachlor
Hexachlorobenzene
Hexachlorobutadiene (HCBD)
Hexachlorocyclohexane
Hexachloroethane
Hexachloronorbornadiene
Hexaconazole
3-Iodo-2-proponyl n-butyl carbamate (IPBC)
Linuron
Malathion
Mercury
Mevinphos
Oxydemeton-methyl
Parathion
Parathion-methyl
Pentachlorobenzene
Pentachloroethane
Pentachlorophenol (PCP)
Permethrin
Propanil
Simazine
Tetrabutyltin
1,2,4,5-Tetrachlorobenzene

Dichloroaniline

1,2-Dichlorobenzene

1,3-Dichlorobenzene

1,4-Dichlorobenzene

Dichloronitrobenzene (all isomers)

2,4-Dichlorophenol

1,3-Dichloropropene

Dichlorprop

Dichlorvos

Dicofol

Dieldrin

Dimethoate

Tetrachloroethylene

Triazophos

Tributyl tin oxide (TBTO)

Tributyl-phosphate

Trichlorfon

1,2,4-Trichlorobenzene

Trichloroethylene

Trichlorophenol (all isomers)

Trifluralin

Triphenyl tin oxide (TPTO)

Triphenyl-phosphate