



Process Guidance

# Inorganic Chemicals

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# **Processes Subject to Integrated Pollution Control**

**IPC Guidance Note  
Series 2 (S2)  
Chemical Industry Sector**

**S2 4.04: Inorganic Chemicals**

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## Executive Summary

This IPC Guidance Note is issued by the Environment Agency as one of a series of guidance notes for processes prescribed for Integrated Pollution Control (IPC) in Regulations made under Section 2 of the Environmental Protection Act 1990 (EPA90). It is a guide on techniques and standards relevant to inorganic chemical processes (excluding acid and halogen manufacture) and processes related to them. It supersedes Her Majesty's Inspectorate of Pollution's Chief Inspector's Guidance Notes IPR 4/16 and IPR 4/18 to IPR 4/25 published by HMSO in 1993.

It will be used by Agency staff, in conjunction with other relevant guidance, in assessing operators' proposals relating to their Authorisations under EPA90. This Note should be used together with separate guidance on monitoring, dispersion methodology and assessment principles for determining Best Available Techniques Not Entailing Excessive Cost (BATNEEC) and Best Practicable Environmental Option (BPEO) to provide a framework for a consistent approach to the regulation of this class of processes regulated under IPC.

The processes covered by this Note are found in Sections 4.5 and 4.6 of the Regulations. Other inorganic chemical processes (acids and halogens) prescribed for IPC are covered by IPC Guidance Note S2 4.03. Petrochemicals and large-volume organic compounds are covered by IPC Guidance Note S2 4.01; batch and fine organic chemicals including pesticides and pharmaceuticals are covered by IPC Guidance Note S2 4.02.

This Note provides brief descriptions of selected processes, best available techniques for pollution prevention and control, and the levels of release achievable by their use. Economic information on example sectors of the inorganic chemical industry is included.



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# 1 Introduction

## 1.1 Scope and status of Guidance Note

This IPC Guidance Note supersedes Her Majesty's Inspectorate of Pollution's Chief Inspector's Guidance Notes IPR 4/16 and IPR 4/18 to IPR 4/25 published by HMSO in 1993. It is issued by the Environment Agency as one of a series of guidance notes for processes prescribed for Integrated Pollution Control (IPC) in Regulations<sup>(1)</sup> made under Section 2 of the Environmental Protection Act 1990 (EPA90). It is a guide on techniques and standards relevant to the processes covered by the Note.

It will be used by Agency staff, in conjunction with other relevant guidance<sup>(2)</sup>, in assessing operators' proposals relating to their Authorisations under EPA90. This Note should be used together with separate guidance on monitoring<sup>(3)</sup>, dispersion methodology<sup>(4)</sup>, and assessment principles for determining Best Available Techniques Not Entailing Excessive Cost (BATNEEC) and Best Practicable Environmental Option (BPEO)<sup>(5,6)</sup> to provide a framework for a consistent approach to the regulation of this class of IPC process.

This Note represents the state of understanding at the time of writing, and includes:

- description(s) of the principal processes covered by the Note;
- the prescribed substances and other substances that can cause harm and are most likely to be released from the processes;
- guidance on best available techniques (BATs) for the control of releases;
- benchmark release levels;
- other environmental standards relevant to the process; and
- information on the economic implications of the relevant pollution control techniques.

An operator should keep up to date with the best available techniques relevant to the process. This Note may not therefore be cited in an attempt to delay the introduction of improved, available techniques, and, except where specifically stated to the contrary, nothing contained herein should be considered prescriptive.

The concepts of BATNEEC and BPEO expressed in the EPA90 and associated Regulations are site-specific. This Note cannot take into account such site-specific considerations. Thus, while operators' proposals should be judged against the benchmark release levels given in this Note, the benchmarks should not be applied as uniform release limits. They are indicative, but not prescriptive, for new processes that are expected to use modern techniques for the prevention, minimisation and abatement of releases.

Where other release levels are proposed for a specific case, comparing them and the benchmark release levels will indicate the degree of technical and economic justification required to be provided by the operator. Conditions in authorisations that relate to permitted releases should ensure that all factors, including those which are site-specific, have been taken into account, and that the legal requirements to use BATNEEC and BPEO are fully satisfied.

Compliance with statutory environmental quality standards or objectives, and with agreed international obligations relating to permitted releases or environmental standards, is mandatory. No discretion is permitted without formal policy approval.

## 1.2 Existing processes

Existing processes should have been upgraded taking into account the criteria included in Articles 4, 12 and 13 of the European Community Directive on the Combating of Air Pollution from Industrial Plants known as the Air Framework Directive (84/360/EEC)<sup>(7)</sup>. Article 13 requires the following points to be taken into account:

- the plant's technical characteristics;
- its rate of utilisation and remaining life;
- the nature and volume of polluting emissions from it; and
- the desirability of not entailing excessive costs for the plant concerned, having regard in particular to the economic situation of undertakings belonging to the category in question.

Most existing processes should have completed their improvement programmes and, subject to the above points, should be achieving the relevant benchmark release levels given in Section 4 or should be closely approaching them. Where this is not so, a timetable for further improving or decommissioning the process should be required.

## 1.3 Processes covered by this Note

This Note covers processes for the manufacture of inorganic chemicals except acids and halogens, which are covered in IPC Guidance Note S2 4.03<sup>(8)</sup>. Most, but not all, are continuous processes and relate most closely to those listed in Sections 4.5 and 4.6 of the Regulations<sup>(1)</sup>. Not all relevant processes operating in the UK can be covered and the Note is not intended to coincide precisely with these sections of the Regulations. Where other prescribed processes are carried on in conjunction with the primary process, reference should be made to the relevant Chief Inspector's Guidance Notes (CIGNs) or IPC Guidance Notes (IPCGNs) and, where appropriate, the Secretary of State's Guidance for Local Authority Air Pollution Control on the ancillary processes insofar as they have potential for releases to the environment.

In the context of this Note 'process' is from receipt of raw materials via production of intermediates to dispatch of finished products.

#### 1.4 Reference conditions used throughout this Note

The reference conditions of substances in releases to air from point sources are: temperature 273 K (0°C), pressure 101.3 kPa (1 atmosphere), no correction for water vapour or oxygen.

These reference conditions relate to the benchmark release levels given in this Note and care should always be taken to convert benchmark and proposed releases to the same reference conditions for comparison. The Authorisation may employ different reference conditions if they are more suitable for the process in question.

To convert measured values to reference conditions see Technical Guidance Note M2<sup>(9)</sup> for more information.

Releases may be expressed in terms of mg/m<sup>3</sup>, g/h, g/t (product) or g/MJ as appropriate.

### 1.5 Standards and obligations

#### 1.5.1 Air quality standards

Statutory Instrument 1989 No 317, *Clean Air, The Air Quality Standards Regulations 1989*<sup>(10)</sup> gives limit values in air for the following substances:

- sulphur dioxide;
- suspended particulates;
- lead; and
- nitrogen dioxide.

Any emission from the process should not result in a breach of the appropriate air quality standard beyond the site boundary.

#### 1.5.2 Air quality objectives

Statutory Instrument 1997 No 3043, *Environmental Protection, The Air Quality Regulations 1997*<sup>(11)</sup> gives air quality objectives to be achieved by 2005 for:

- benzene;
- 1,3 - butadiene;
- carbon monoxide;
- lead;
- nitrogen dioxide;
- PM<sub>10</sub>; and
- sulphur dioxide.

#### 1.5.3 The UNECE Convention on Long-Range Transboundary Air Pollution<sup>(12)</sup>

Under this Convention, a requirement further to reduce SO<sub>2</sub> emissions from all sources has been agreed. The second Sulphur Protocol (Oslo, 1994) obliges the UK to reduce SO<sub>2</sub> emissions by 80% (based on 1980 levels) by 2010. Negotiations are now under way which could lead to a requirement further to reduce emissions of NO<sub>x</sub> and volatile organic compounds (VOCs).

#### 1.5.4 Volatile Organic Compounds

'Reducing Emissions of VOCs and Levels of Ground Level Ozone: A UK Strategy'<sup>(13)</sup> was 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. A 65% reduction is forecast for the chemicals sector, based on the application of BATNEEC

#### 1.5.5 Water quality standards

Statutory Instrument (1989) No 2286<sup>8</sup>, *The Surface Waters (Dangerous Substances Classification) Regulations* give the annual mean concentrations limit values for certain substances in receiving waters. These include cadmium and mercury.

#### 1.5.6 Groundwater protection

The principles, powers and responsibilities for groundwater protection in England and Wales, together with the Agency's policies in this regard, are outlined in the Agency's document "Policy and Practice for the Protection of Groundwater" (PPPG)<sup>(14)</sup>. This outlines the concepts of vulnerability and risk and the likely acceptability from the Agency's viewpoint of certain activities within groundwater protection zones.

The EC Directive on the Protection of Groundwater against Pollution Caused by Certain Dangerous Substances (80/68/EEC)<sup>(15)</sup> imposes an obligation on Member States to prevent the introduction into groundwater of List I substances and to limit the introduction of List II substances so as to prevent pollution of groundwater. List I and List II substances are described in Appendix 1 of the PPPG. The Directive is at present implemented by, *inter alia*:

- Part I of the Environmental Protection Act 1990, which requires Authorisation of IPC processes;
- Part II of that Act, which requires the management of controlled wastes;
- Regulation 15 of the Waste Management Licensing Regulations 1994, which requires the Agency to observe the provisions of the Groundwater Directive when issuing waste management licences; and
- Part II of the Water Resources Act 1991, which make it an offence to discharge polluting matter to controlled

waters, except in accordance with a Consent issued by the Agency.

The Government is introducing new Groundwater Regulations to provide additional protection and complete the transposition of the Groundwater Directive. In addition to those processes controlled for IPC, these Regulations are intended to relate primarily to activities where List I and II substances are either deliberately discharged, or where there is a risk of discharge occurring, for example, as a result of spillages or leaks. The Regulations will provide for prior investigation of the potential effects of discharges on groundwater; the Authorisation of disposal or tipping to land and Consents to discharge to groundwater; the serving of Notices by the Agency to prohibit activities or to apply conditions; the recognition the importance of Codes of Practice; and provisions for cost recovery by the Agency.

Two key aspects of the Groundwater Directive are the need for the following:

- **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 Agency is likely to require a map of the proposed disposal area; a description of the underlying geology, hydrogeology and soil type, including the depth of saturated zone and quality of groundwater; the proximity of the site to any surface waters and abstraction points, and the relationship between ground- and surface waters; the composition and volume of waste to be disposed of; and the rate of planned disposal.
- **Requisite surveillance.** This will also vary from case to case, but will include monitoring of groundwater quality and ensuring that the necessary precautions to prevent groundwater pollution are being undertaken.

The Directive states 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 Agency where this is being considered as a justification for such discharges. The Agency is obliged to take account of these requirements for IPC processes and, where there is an activity that represents a potential risk to groundwater, may request further investigations (see Section 6.6).

## 2 Processes, potential release routes and specialised techniques for controlling releases

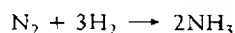
### 2.1 Introduction

The significant processes in the subsector are briefly described and the release routes of pollutants from them are indicated. The control techniques that are considered to be BAT for the process are listed either by reference to Section 3 on general techniques or, where they are special to the subsector concerned, they are described. Release levels achievable by the use of the techniques are provided in Section 4 for each group of related processes as benchmarks. They should not be applied as uniform release limits.

### 2.2 Ammonia production

#### 2.2.1 Introduction

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



Nitrogen is extracted from air, either by burning out the oxygen or by air liquefaction.

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
- ⊗ other sources, such as by-products from plants making other chemicals.

Current production in the UK is based on steam reforming of natural gas and on the use of hydrogen produced as a by-product of carbon monoxide manufacture.

The processes are highly integrated to optimise material and thermal efficiencies. Three main alternatives are described.

#### 2.2.2 Steam reforming: conventional

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 2.1.

#### (a) Desulphurisation

To avoid poisoning the reformer catalysts, sulphur compounds in the natural gas feedstock are removed to below 0.15 mg/m<sup>3</sup>. For this purpose the gas is heated to 350–400°C, usually in the primary reformer, and then passed to the convection section, together with a small hydrogen stream across a cobalt-molybdenum catalyst. Here the sulphur compounds are hydrogenated to hydrogen sulphide and then adsorbed onto 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.

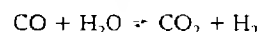
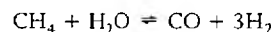
#### (b) Primary reformer

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°C.

The amount of steam is given by the process steam to carbon molar ratio (S/C ratio), which should be around 3 for the BAT reforming process. The optimum ratio depends on several factors, such as feedstock quality, purge gas recovery, primary reformer capacity, shift operation and the plant steam balance.

The reformer catalyst is based upon nickel deposited on a porous alumina support. The catalyst is replaced approximately every four years.

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

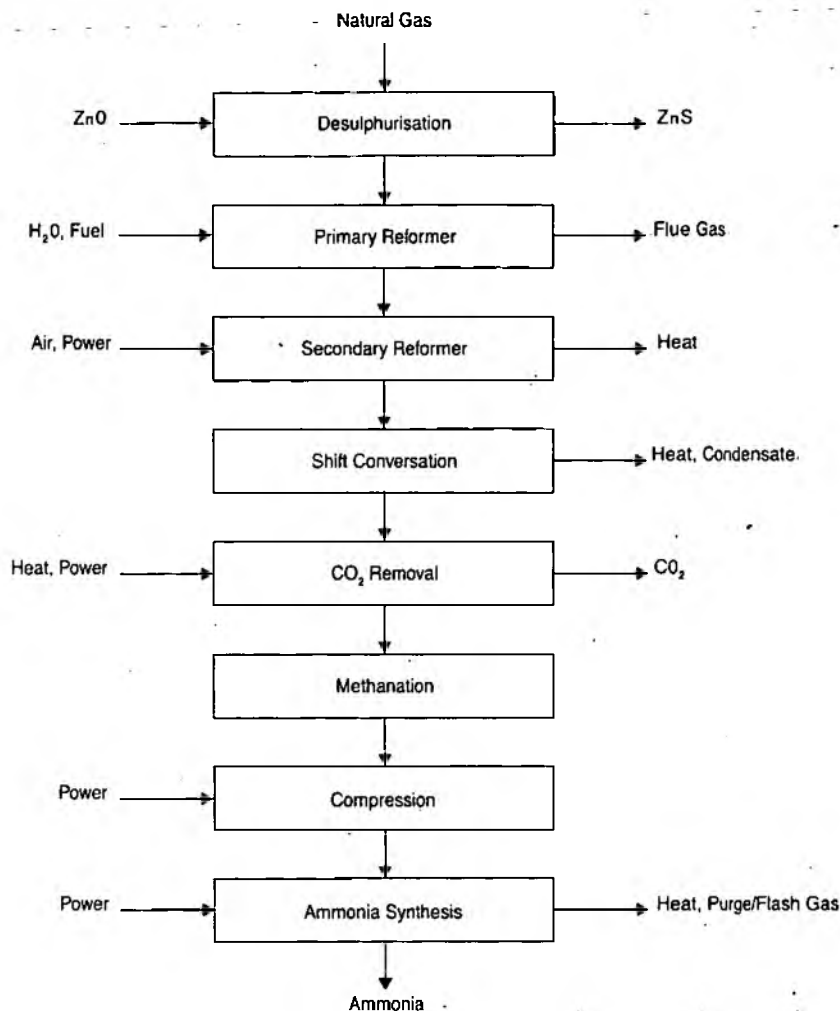


The process is endothermic and energy is supplied by firing in a radiant furnace. Part of the total natural gas supplied to the plant is used as fuel in the furnace together with purge gas from the synthesis stage. The flue gases, at a temperature of 1000–1100°C, are used to provide heat for a number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

#### (c) Secondary reformer

Only 30–40% of the hydrocarbon feed is reformed in the primary reformer because of the chemical equilibria at the actual operating conditions. The temperature must be raised to increase the conversion and this is achieved in the secondary

Figure 2.1 Steam/air reforming process for ammonia



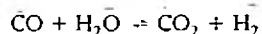
reformer by combustion of the gas with process air, which also provides nitrogen for the final synthesis gas.

The process air is compressed to the reforming pressure, heated further to 600°C in the primary reformer convection section and then passed over a nickel-containing catalyst. The reformer outlet temperature is around 1000°C and up to 99% of the hydrogen feed (to the primary reformer) is converted.

The process gas is cooled to 350–400°C in a waste heat steam boiler or boiler/superheater downstream from the secondary reformer.

#### (d) 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:



In the high temperature-shift (HTS) conversion, the gas is passed through a bed of iron oxide/chromium oxide catalyst at around 400°C. The gas is 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%.

#### (e) Condensation

The process gases are cooled, usually by heat exchange with other process fluids for heat recovery, to condense out the water vapour. The process condensate is the main source of liquid effluent from ammonia plant.

The heat released during cooling/condensation is used for:

- the regeneration of the CO<sub>2</sub> scrubbing solution;
- driving an absorption refrigeration unit; and
- boiler feedwater preheat.

#### (f) Carbon dioxide absorption

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

- physical absorption in a solvent;
- chemical reaction with a reagent; or
- physical adsorption.

Using physical absorption, the solvent, such as methanol, is primarily regenerated by reducing the pressure and allowing the carbon dioxide to desorb.

With the chemical reagent process, heat is required to break the chemical bond and this is a major use of low-pressure steam. The most widely used reagent is monoethanolamine solution with inhibitors to protect against excessive reagent degradation and corrosion.

Pressure swing adsorption (PSA) relies on the use of selective adsorbents. Components of the mixed gas stream are adsorbed at high pressure and then desorbed by depressurisation, and possibly purging, in a cyclic process. PSA systems are particularly appropriate in cases where it is necessary to remove excess nitrogen as well as carbon dioxide.

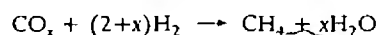
For new ammonia plants the following CO<sub>2</sub> removal processes are currently regarded as BAT:

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

Residual CO<sub>2</sub> concentrations are in the range of 100–1000 ppmv.

#### (g) Methanation and final purification

Whilst most carbon dioxide is removed in the previous stage, residual oxides of carbon are reduced to a few parts per million by methanation over a supported nickel catalyst at 300–400°C. This is required to prevent poisoning of the synthesis catalyst. The reaction is:

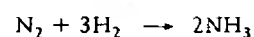


Other purification steps can include:

- dehydration with molecular sieves; and
- cryogenic treatment to remove nitrogen, methane and inerts, eg argon.

#### (h) Ammonia synthesis

The synthesis of ammonia takes place on a porous catalyst containing ferrous and ferric oxides with promoters such as potassium, aluminium, calcium and magnesium oxides, and at pressures usually in the range of 100–250 bar and temperatures in the range of 350–550°C, according to the reaction.



The synthesis loop is fed by the main compressor, whilst the process gas is circulated within the loop by a recirculation compressor.

Ammonia synthesis is exothermic and is usually operated at sufficiently high temperatures to raise high-pressure steam.

Only 20–30% is reacted per pass in the converter due to the unfavourable equilibrium conditions.

Ammonia product is condensed from the gas by heat exchange with cooling water or air, and finally in condensers served by an ammonia refrigerant system before transfer to storage.

Synthesis gas is normally added upstream of the final condensers so that water and other minor impurities are washed out with product ammonia.

The chilled gas from the ammonia separation passes through a heat exchange train and the circulating compressor before returning to the conversion catalyst beds.

A purge is taken off the loop to prevent the build-up of inerts such as methane or argon. The purge gas is usually treated, by washing with water or by chilling, to recover ammonia and is then consumed as a fuel gas in the primary reformer. Recovery of hydrogen by pressure swing adsorption or the use of cryogenic schemes to recover many components are also practised commercially.

Steam reforming ammonia plants have high-level surplus heat available for steam production in the reforming, shift conversion and synthesis sections, and in the convection section of the primary reformer. Most of this heat is used for high-pressure steam production for use in turbines for driving the main compressors and pumps and as process steam extracted from the turbine system.

A modern steam reforming plant can be made energy self-sufficient if necessary but usually a small steam export and electricity import are preferred.

#### (i) Storage

Refer to Section 2.3.12.

#### 2.2.3 Steam reforming: excess-air secondary reforming

Some processes are designed for reduced primary reforming by moving some of the duty to the secondary reformer because of the marginal 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 according to 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 means that increased internal firing 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. This means increased compression capacity and energy. The process air compressor is usually driven by a gas turbine with the exhaust gas from the turbine being 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.

#### 2.2.4 Non-fired primary reformer/autothermal reforming

A reduction of environmental emissions 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 twostage 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.

#### 2.2.5 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.

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, must currently be regarded as best practice for new plants using steam reforming. Adaptation of conventional plants would be expensive and difficult due to their very tightly integrated steam/power systems.

#### 2.2.6 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: 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, eg 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.

### 2.2.7 Control of releases arising from ammonia production

#### (a) Control of gaseous releases

##### 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<sup>(7)</sup>).

### Carbon dioxide

The quantity of carbon dioxide removed from the process gas depends on the process selected. Some beneficial uses are possible, for example, export to the brewing and soft drinks industry.

#### Ammonia

Ammoniated vents occur from several sources and the ammonia is controlled by absorption, condensation, incineration and containment. These techniques are discussed in Section 2.3.12

#### Containment

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.

#### (b) Control of aqueous releases

Steam stripping techniques are used to remove volatile organic components dissolved in aqueous effluent streams. Very often gaseous effluent streams requiring further treatment can be formed. The BPEO of the stripping process should be justified in the application.

Process condensate should be stripped to reduce the ammonia content to 10 mg/l, unless the condensate passes to a treatment plant in which recovery is jointly performed on a number of ammoniated liquors.

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. Contaminated effluent steam strippers are prone to plugging and sequestering agents are frequently used to prevent calcium deposition.

The potential releases into water arise from inadequate stripping performance. Steam stripping typically removes about 99% of the ammonia from a waste stream.

### (c) Control of waste to land

Sludges will be generated by separation of fines from effluent streams.

Solid wastes containing potentially acidic materials should be neutralised prior to disposal to landfill.

### 2.2.8 Performance data for BAT processes

Studies carried out by the European Fertiliser Manufacturers Association have generated the data in Tables 2.1 and 2.2 for raw material input requirements and expected emissions levels for BAT ammonia production plant.

**Table 2.1 Production input requirements.**

All values in GJ/tonne (HHV<sup>(a)</sup>)

	Feedstock	Fuel	Total Energy	Air (kg/kg NH <sub>3</sub> )
Conventional reforming	24.5	8–10	32.5–34.5	1.1
Excess air reforming	26.0	6–8	32.0–34.0	1.65
Autothermal reforming	27.5	4–8	31.5–35.5	2.2

<sup>(a)</sup> Higher heat value.

**Table 2.2 Performance data for BAT processes.**

Solvent consumption, CO <sub>2</sub> removal unit	0.01–0.02 kg/tonne NH <sub>3</sub>
Carbon dioxide production	1.15–1.30 kg/kg NH <sub>3</sub>

Studies for the EC BAT Reference Document for Ammonia are summarised in Table 2.3

**Table 2.3 Performance data for BAT processes.**

	Advanced conventional reforming	Excess air reforming	Autothermal reforming
Nox to atm. (mg/Nm <sup>3</sup> ) (g/t NH <sub>3</sub> )	157 320	90 290	100 175
Net energy consumption (GJ/t NH <sub>3</sub> (LHV <sup>(b)</sup> ))	29.2	28.9	29.5
NH <sub>3</sub> to water (g/t NH <sub>3</sub> )	28	negligible	80

<sup>(b)</sup> Lower heat value

The choice of process may depend on site-specific factors as well as achievable performance.

## 2.3 Processes using or releasing ammonia

### 2.3.1 Introduction

This section contains basic information on some of the currently significant process options for the manufacture of chemicals involving the use of ammonia or resulting in the release of ammonia into the air. Processes involving the use of these chemicals are diverse and therefore not all individual processes are covered. Descriptions are given of typical waste streams to all media resulting from these processes.

Production units for these chemicals range from large dedicated facilities to small multi-purpose chemical plants that are run on a campaign basis. This diversity significantly affects the magnitude, pattern and relative importance of both the continuous (eg aqueous effluent streams from distillation columns) and the intermittent discharges (eg plant wash-downs).

In several of the following processes, ammonia releases to air are not diluted by inerts. Concentration levels, as given in Section 4.1, are inappropriate to these streams. The release should be related to the mass of product produced or processed.

### 2.3.2 Ammonia recovery

#### (a) Process

Ammonia is recovered, essentially by stripping, from weak solutions resulting from other processes. Sometimes the gas, stripped from the weak solution, may be dried and used in other processes, but more often it is recovered to make strong ammonium hydroxide (s.g. 0.880).

The weak solution is heated by heat exchange with stripped liquor and the ammonia is removed by steam stripping. In order to achieve maximum recovery of ammonia, alkalis such as calcium hydroxide or sodium hydroxide are added to raise the pH to about 9. The mixed gas stream containing ammonia and steam is then cooled to condense out an ammonia solution. As with other processes dissolving ammonia in water, it is necessary to cool below ambient temperature to reduce the vapour pressure of ammonia above the solution. Typically a temperature of about 5°C is needed if 0.880 ammonia solution is to be produced.

A tail gas scrubber is provided on the final outlet to air to minimise releases.

Depending on the process the recovered ammonia solution may be treated with activated carbon to remove contaminants.

**(b) 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**

- Active carbon filters.

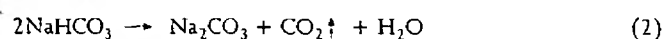
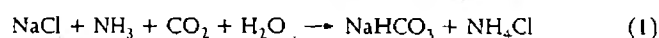
**2.3.3 The solvay ammonia soda process****(a) Process**

The Solvay process consists of three main parts: a calcium hydroxide producing section, a brine processing section (in which sodium hydrogencarbonate is produced), and a boiler

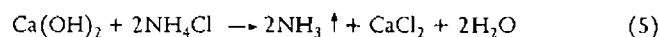
house (large combustion plant). The first and last of these are covered by IPC Guidance Notes S2 3.01<sup>(18)</sup> and S2 1.01<sup>(17)</sup> respectively. A flowchart of the process is shown in Figure 2.2.

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:

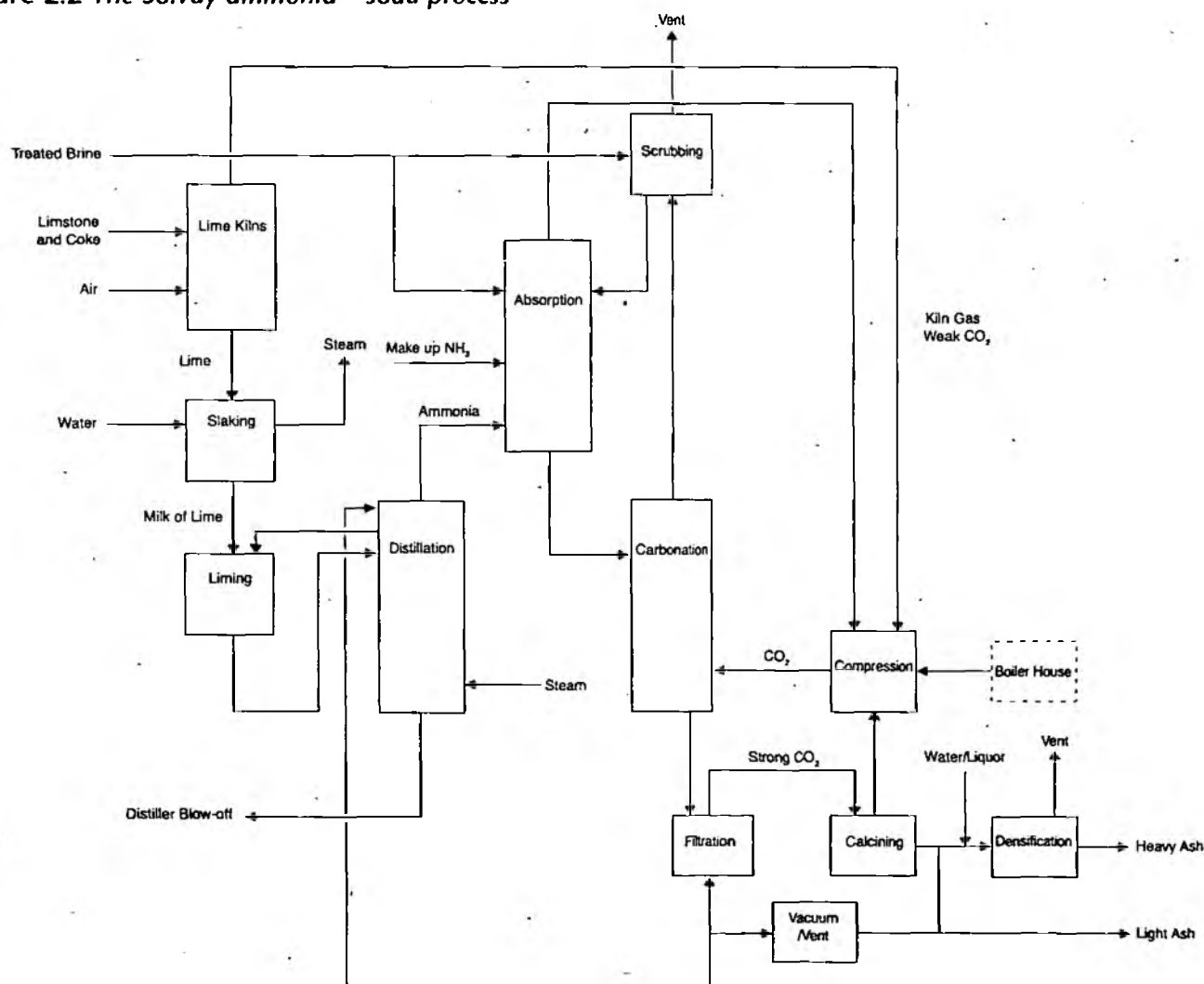


Subsidiary reactions are:



The carbon dioxide and ammonia liberated in equations (2), (3) and (5) are collected and recycled to the initial reaction. Theoretically all the ammonia used is regenerated and recycled.

**Figure 2.2 The Solvay ammonia – soda process**



but in practice there are losses, which are replaced with ammonia make-up. The make-up ammonia will contain hydrogen sulphide, which is required to help prevent plant corrosion. If the ammonia used has insufficient hydrogen sulphide, then sodium hydrogen sulphide is added.

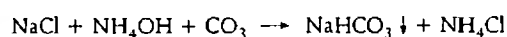
The rest of the carbon dioxide needed in the process comes from the burning of limestone in shaft kilns using coke as the fuel. The carbon dioxide generated is mainly used in the carbonation section of the process but up to 10% of the gas may be discharged to air. Some of the carbon dioxide may be used for the carbonation of distiller bottom off-take liquor, and this will reduce the amount of kiln gas bled to air. The calcium oxide produced is hydrated in a rotary slaking plant before being converted into 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 ammonia, hydrogen sulphide and, additionally, some carbon dioxide from the main emissions from the process. Some of the brine is used for scrubbing other vents.

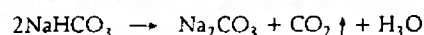
The sodium chloride solution then goes to absorbers of the ammonia-rich gases that have arisen out of the distillation of limed liquor from the filtrate of the intermediate product (sodium hydrogencarbonate). This absorption is an exothermic reaction so the liquor is removed part-way through the ammonisation, cooled and then returned to the absorber. The final liquor is stored in intermediate vats as "strong vat liquor" (SVL) before being cooled and passed to the carbonation stage.

Several towers are provided for carbonation and are used alternately on a making and a cleaning cycle. In the cleaning cycle, the SVL is passed counter-current to lime kiln gases from the calcium hydroxide burning plant. The agitation caused by bubbling the gas into the brine dissolves sodium hydrogencarbonate scale deposited in the tower during the making cycle. The carbonated SVL passes through a degasser and is pumped into the making tower.

The carbonated SVL enters the top of the making tower and on its passage down encounters carbon dioxide being fed into the tower in two places: half-way down lime kiln gas enters and at the bottom mixed carbon dioxide. The latter is a mixture of lime kiln gas and the strong gas resulting from the decomposition of the sodium hydrogencarbonate. The tower is cooled internally to maximise the absorption of carbon dioxide and hence the precipitation of sodium hydrogencarbonate:



The precipitated sodium hydrogencarbonate is separated from the liquor, washed and fed to steam-heated 'secheurs' where it is decomposed to sodium carbonate:



The gas so generated is cooled to condense out the water, which is used to wash the filter cake. The residual strong carbon dioxide is, after scrubbing with incoming sodium chloride

solution, returned to the bottom of the carbonation making tower.

The filtrate, from the 'secheurs', contains ammonium chloride, ammonia and carbon dioxide. It is taken to the distillation section of the plant where ammonia and carbon dioxide are stripped out in the top of the column. The liquors are then mixed with slaked calcium hydroxide to liberate ammonia from the ammonium chloride. This ammonia is stripped out using live steam. The ammonia and carbon dioxide pass to the absorber towers. A small ammonia make-up is required.

Solids in the residual liquor are removed by settling. The residual liquor is neutralised with either acid or carbon dioxide. If the latter is used then the liquor may be subject to further settlement in lagoons. Whichever route is used, the final supernatant liquor is discharged to water. If settling lagoons follow carbonation, then the residual solids are disposed of to land.

The sodium carbonate made by this route is known as 'light ash' and may be converted into 'heavy ash'. The light ash is hydrated with a sodium carbonate solution to produce the monohydrate, and then dehydrated to produce a pseudomorph of sodium carbonate. Particulate emissions from the 'secheurs' are controlled with dust arresters, which may be scrubbers.

The product is screened and oversize material crushed before conveying to storage silos for final packing or loading into tanker lorries. All potential release points to air, such as screens, conveyors, etc, are protected by bag filter units.

## (b) Potential release routes from the solvay ammonia soda process

### Releases to air

- Ammonia, carbon dioxide and hydrogen sulphide from vents on absorbers, scrubbers and distillation units.
- Particulate from drying, storage and handling of product.
- Ammonia and hydrogen sulphide from vents on ammonia storage tanks.
- Hydrogen sulphide from vents on sodium hydrogen sulphide storage tanks.
- Carbon monoxide, carbon dioxide, oxides of nitrogen, oxides of sulphur and particulate matter from calcium hydroxide burning and slaking.

### Releases to water

- Distiller bottom off-take liquor containing phenols, cyanides,  $\text{CaCl}_2$ ,  $\text{NaCl}$  with an ammonia/ammonium content. Its composition is roughly 10%  $\text{CaCl}_2$ , 5%  $\text{NaCl}$ , and ammonia/ammonium amounting to 1 to 1.5 kg/tonne of product.
- Aqueous discharges from scrubbers and cooling water systems.

**Releases to land**

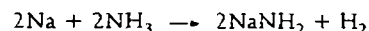
- Solids from clarification of distiller bottom liquor.
- Waste materials including contaminated product.

**2.3.4 The sodamide process****(a) Process**

Sodamide is sometimes produced for sale and sometimes for direct use. Two methods are used: one is solvent-based and the other, more usual, process is a dry process using molten sodium.

Sodium is melted under a nitrogen blanket in a sealed vessel. The reaction vessel is fitted with overpressure protection and any emergency relief system is vented to a containment vessel from which the residual gases discharge at high level.

Ammonia is fed into the reactor at controlled rates where it reacts with the sodium to form sodamide. The exothermic reaction is controlled by regulating the rate of addition of ammonia. In addition cooling is applied to the reactor. The reaction is:



An excess of ammonia is used and this, together with hydrogen generated in the reaction, is burnt via a flare. Particulate matter is removed from the gas stream before it is fed via a seal pot to the flare stack. To minimise entrainment of sodamide in the gas stream and to prevent any ingress of air, forced extraction is not used.

To maximise destruction of ammonia, a supplementary flame of natural gas is used. This 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 to prevent addition of ammonia to the reactor when the flare stack is not fully operational.

The use of water on the plant is limited for safety reasons; both molten sodium and sodamide react violently with water.

Prolonged contact of sodamide with dry air can give rise to the formation of peroxides.

Where the product is isolated, solidified and packed it is conveyed using nitrogen, which is recirculated, but some nitrogen is 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. Such material will require decontamination in special equipment. Steam and water spray techniques are used, resulting in a sodium-hydroxide-contaminated liquid effluent. Oil used for sealing the reaction vessel will, after some time, be contaminated with sodamide and need replacement. The contaminated oil should preferably be treated on-site to remove any sodamide, rather than disposed of via a waste contractor.

**(b) Potential release routes from the sodamide process****Releases to air**

- Ammonia and sodamide from pressure relief.
- Ammonia and oxides of nitrogen from flare.

**Releases to water**

- Sodium hydroxide from water scrubbing of vented nitrogen and washing of equipment

**Releases to land**

- None.

**2.3.5 Nickel catalyst manufacture****(a) Process**

An aqueous nickel solution is prepared in a stirred vessel by mixing ammonia solution, nickel and ammonium salt. The vessel is maintained under reduced pressure by a fan that exhausts to atmosphere.

Extruded alumina is dried in an indirect gas-fired heater. The dried alumina is mixed with the prepared nickel solution to impregnate the alumina with nickel ions. The ammonia liberated in the reaction is treated in a wet scrubber.

Excess nickel solution is removed by vacuum filter and recycled for the next batch. The resultant solid is hot-air dried before heat treatment. The product is then classified to give the required product agglomerate size. Oversize and undersize material that cannot be recycled within the process is sent for off-site nickel recovery.

Aqueous streams and spent scrub liquors are treated by passing 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.

**(b) Potential release routes from nickel catalyst manufacturing****Releases to air**

- The main releases to air are dust and ammonia gas from vessel ventings.
- All ammonia-laden streams are passed to wet scrubbers before discharge to atmosphere.
- Bag filters are employed to remove particulate matter.

**Releases to water**

- The main releases to the aqueous environment are ammonia and nickel.

### Releases to land

- Spent ion exchange resin, bag filters and waste extrudate sweepings are exported to landfill.

## 2.3.6 Biochemical processes using ammonia

### (a) Processes

This is a class of process that is quite diverse, 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 water solution of trace elements, contained in a deep vessel. The micro-organism is fed with a carbohydrate. Air mixed with ammonia gas (of the order of 200 kg/h of ammonia) is blown into the bottom of the reactor.

When the reaction has progressed far enough, the mixture is withdrawn, heated to stop further reaction and the product filtered off. The filtrate is discharged to a treatment plant.

In most of these processes, due to the depth of the solutions used and the need to maintain steady temperatures, the ammonia injected is adequately absorbed and a scrubber is not required.

### (b) 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<sub>5</sub>.

#### Releases to land

- None.

## 2.3.7 Manufacture of ammonium hydrogencarbonate/ammonium carbonate

These are considered together, as both involve the reaction of carbon dioxide with ammonia. Additionally, liquor from the ammonium hydrogencarbonate process can be used as a raw material in the ammonium carbonate process.

For ammonium hydrogencarbonate, carbon dioxide is absorbed in ammonium hydroxide solution. Three ammonium-hydroxide-containing vessels are used in series, with the first being the making vessel and the second and third absorbers to maximise carbon dioxide utilisation.

Carbon dioxide, generated by heating liquefied gas, is passed into the ammonium hydroxide solution until a sample withdrawn from the vessel indicates that the reaction is complete. Excess carbon dioxide is passed through subsequent

absorbers and any remaining after this will be released to air together with ammonia stripped from the solution.

The resultant ammonium hydrogencarbonate slurry is thickened in a hydroclone before being centrifuged and dried; oversize material is ground and the product bagged. The drying is carried out with steam-heated air and this together with extracted air from the grinding operation is filtered before discharge to air.

Excess mother liquor from this process can be used in the ammonium carbonate process as a source of ammonia, carbon dioxide and water.

Commercial ammonium carbonate, which is a mixture of ammonium carbonate and ammonium hydrogencarbonate, is produced by reacting ammonia gas and carbon dioxide with steam.

The hot gases are ducted to a number of condensers arranged in parallel. At the start of a cycle the condenser is purged. The purge gas is vented to atmosphere.

Condensation continues until the layer of product is sufficiently thick to reduce the heat loss to the level where condensation ceases. At this stage the supply of gas to the condenser is stopped, the vessel opened and the ammonium carbonate dug out.

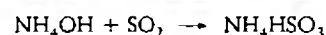
The product is milled to a uniform size before packaging. Excess mother liquor from ammonium hydrogencarbonate production can be used as an additional source of raw materials; steam stripping allows the recovery of ammonia and carbon dioxide. The residual liquor is discharged to drain.

## 2.3.8 Manufacture of other ammonium salts

### (a) Various processes

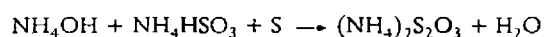
Ammonium hydroxide is used in the manufacture of other ammonium salts such as ammonium bisulphite, ammonium thiosulphate, and salts such as ammonium bromide, whilst gaseous ammonia is used in the production of ammonium phosphates. In all these cases whilst ammonia may be emitted there is also the possibility of releasing acid gases.

For ammonium bisulphite the processes may be continuous or batch. The bisulphite is formed by reaction between aqueous ammonium hydroxide and sulphur dioxide:



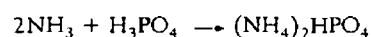
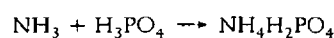
The off-gases, containing ammonia and oxides of sulphur, pass to an irrigated mist eliminator where the ammonia is absorbed and returned to the process. The residual off-gases are treated in a sodium hydroxide tail gas scrubber. The sodium hydroxide scrubber may also receive acidic off-gases from other sulphur dioxide absorption systems and be followed by an electrostatic precipitator. Alternatively the residual off-gases may be used in other reactions that require sulphur dioxide. The product liquor is polished, filtered and transferred to storage.

Ammonium thiosulphate is formed by the reaction of aqueous ammonia, sulphur and ammonium bisulphite:



The vent gases from the reactor are scrubbed with water and ammonium bisulphite in 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 a build-up of impurities.

Monoammonium phosphate and diammonium phosphate are made by injecting gaseous ammonia into phosphoric acid to produce a slurry of crystals of the respective products:



The off-gases pass to a phosphoric acid scrubber which absorbs excess ammonia. The scrubber liquor returns to the reactor. The slurry is centrifuged to remove the product, which is dried prior to packaging for sale. The filtrate is returned to the reactor. A bleed is taken off this recycle to prevent a build-up of impurities and is sold into the fertiliser market.

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 will 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 release is insignificant.

#### (b) Potential release routes from the manufacture of ammonium compounds

Details of potential release routes from ammonium carbonate/ammonium hydrogencarbonate and ammonium salts production are given below.

##### Releases to air

- Ammonia from vents.
- Carbon dioxide, oxides of sulphur, hydrogen fluoride and ammonia from absorbers.
- Ammonium salts in particulate form from dryers, handling, and sizing operations.
- Ammonia, carbon dioxide, ammonium hydrogencarbonate and ammonium carbamate during start of condensers in ammonium carbonate production.
- Ammonia from vapour pressure of ammonia above ammonium carbonate. Losses can occur during digging

out of condensers and milling of product.

##### Releases to water

- Mother liquor from ammonium hydrogencarbonate process containing ammonia.
- Process liquors from scrubbers that may contain ammonia, sodium sulphite and sodium sulphate.

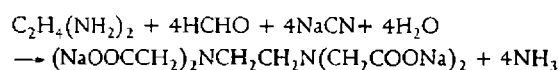
##### Releases to land

- Solids and activated carbon from polish filters on ammonium bisulphite and thiosulphite production.
- Metal sulphides and sulphur from filtration of ammonium thiosulphate liquors.

#### 2.3.9 Chelating agent manufacture (EDTA and related compounds)

##### (a) Process

The sodium salts of ethylenediamine tetraacetic 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:



Ammonia is released as a by-product of the reaction and boils off continuously. The ammonia is arrested by condensation and/or multi-stage scrubbers using cooled recirculated water as the scrubbing medium for the first stage. Back-up scrubbers are used to reduce the release to air and these may be 'once-through' water scrubbers. Approximately 180 kg of ammonia is recovered, for sale as aqueous ammonia solution, for every tonne of EDTA produced.

Some of the ammonia is cyanomethylated to form salts of nitrilotriacetic acid (NTA) and other compounds. These side-products remain in the product unless the free EDTA is precipitated by acidification.

With analogous products, a condenser is used to reflux the amines.

An alternative commercial process, the Singer synthesis, involves reaction of hydrogen cyanide, formaldehyde and ethylenediamine to form insoluble (ethylenedinitrilo) tetraacetoneitrile, 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, for example EDTA, is separated by centrifuge. The filtrate, and any washing, is neutralised before discharge to liquid effluent.

**(b) Potential release routes 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 scrubbers.
- Filtrate from production of the acid form of the chelates, containing sodium sulphate, sodium chloride and chelating agents and, potentially, traces of amines, formaldehyde and cyanide.
- The impact of aqueous discharges containing chelating agents on the immediate environment should be carefully assessed as chelating agents are capable of mobilising and maintaining heavy metals in solution.

*Releases to land*

- None.

**2.3.10 Zeolite manufacture****(a) Process**

Solutions of sodium aluminate, sodium hydroxide and sodium silicate are added together to form a zeolite. To the resulting solution, sodium aluminate, sodium silicate and a solution of aluminium sulphate are added. The soda Y zeolite precipitates out and is recovered as a slurry from a filter, the filtrate being recycled within the process. The slurry is further filtered and washed before passing to intermediate storage.

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 is fed to a gas-fired dryer, the vent passing to atmosphere via a bag filter. The dried product is treated in a gas-fired calciner. The vent stream containing combustion gases, ammonia and ammonia oxidation products passes to atmosphere via a bag filter.

**(b) Potential release routes from the manufacture of zeolites***Releases to air*

- Main releases to air are ammonia and particulates from the calciner, dryer vent, product and ammonia storage.
- Releases to water
- Main releases to water are ammonium and sodium salts.

*Releases to land*

- General solid waste from manufacturing process.

**2.3.11 Processes using ammonia as a solvent****(a) Processes**

Several processes use ammonia as a solvent in the manufacture of organic chemicals. The potential releases to air are mainly the ammonia used (the products being fairly complex non-volatile compounds).

Processes of this type are normally carried out in a sealed vessel, fitted with a bursting disc or pressure relief valve. If a bursting disc is used, this discharges into a containment vessel from which residual gases are vented at high level. If a pressure relief valve is used, then the gases vented from it are scrubbed. The vessel also has a vent to a water scrubber.

Ammonia is stored in a pressure vessel from which it is withdrawn using the vessel's pressure as the driving force. It is then discharged into the reaction vessel, the drop in pressure resulting in adiabatic cooling to a liquid at roughly -33°C. The reactants may either be pre-charged into the reactor or added after the ammonia addition. Other reactants may be added later to complete the reaction.

Ammonia evaporating from the 'solvent' is collected and returned to the reactor via a reflux condenser, which has a back-up scrubber system. Alternatively the ammonia is collected in a water adsorption system to generate ammonium hydroxide solutions.

For some products alternative processing may involve partial evaporation of ammonia by pressure reduction and neutralisation of the remaining solvent to precipitate the product. The product is separated by filtration and washed. The filtrate and washing form part of the aqueous effluent.

BATNEEC for recovery of ammonia, either by refrigeration and recycle with back-up scrubbers, or by a water absorption system producing ammonium hydroxide for re-use or sale, will be dependent on the scale of the process and the demand for ammonium hydroxide.

**(b) Potential release routes from processes using ammonia as a solvent***Releases to air*

- Ammonia from scrubbers, pressure relief and from vents on ammonium hydroxide tanks.

*Releases to water*

- Ammonium salts, alkali-metal salts and trace organics from acidification of intermediate products.
- Alkali-metal salts from cleaning of drums that have contained sodamide or other materials.



**Releases to land**

- None.

**2.3.12 Control of ammonia releases****(a) Ammonia safety and handling**

The storage of anhydrous ammonia is covered by an HSE guidance document HSG30<sup>(19)</sup> which details basic requirements for the design of spherical and cylindrical pressure vessels and essential fittings for safe operation, together with certain operational matters.

Three methods are currently used for storage of anhydrous ammonia, the choice primarily depending on the quantity to be stored:

- Storage at ambient temperature and equivalent pressure in cylindrical vessels for relatively small quantities, as practical manufacturing and transport considerations limit the size of the vessel.
- Storage under pressure in spherical vessels normally for storage of 500 to 3000 tonnes.
- Storage at atmospheric pressure ammonia may be stored at atmospheric pressure by reducing the temperature to -33°C and stored in cylindrical flat-bottomed tanks; this method of storage is considered economical when quantities in excess of 5000 tonnes are involved.

Information on storage and offloading is also available in company publications:

The following safety points should be noted when dealing with ammonia:

- Ammonia gas is pungent and colourless and serves as its own warning agent; the detectable odour limit for ammonia is 5 ppm by volume.
- 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°C.

**(b) Absorption with water**

Commercial scrubber systems include those based on packed columns or trays and venturi or jet scrubber types. The dissolution of ammonia in water is highly exothermic.

The scrubber liquor is a potential waste stream. This can be stripped with steam or air to recover the ammonia for beneficial use.

If high concentrations of ammonia are required in the scrubber liquid effluent, so that it can be used beneficially elsewhere, common techniques include:

- Use of a cooler or recirculating liquor;
- Multiple stages if the equipment design requires liquid recirculation; and
- ⊗ Use of elevated pressures.

**(c) Absorption in reagents**

Use of sulphuric acid as the absorbent generates an ammonium sulphate solution, which can be utilised in the fertiliser market.

**(d) Condensation**

Ammonia condenses at around -33°C at atmospheric pressure. At elevated pressures of waste gas, ammonia can be condensed by refrigeration. The degree of ammonia recovery depends on the pressure of the waste gas and the temperature to which it is cooled.

**(e) Incineration**

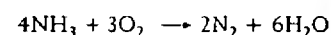
Ammonia is combustible but has a relatively narrow flammability envelope of 15-25% in air.

Incineration typically needs to be supported by the combustion of other components, either if present in the waste gas or by an auxiliary burner. Incineration of ammonia leads to the production of NO<sub>x</sub>.

In general, condensation and wet scrubbing are preferred as a means of controlling ammonia emissions to atmosphere. Emergency or start-up vents may be an exception, where properly designed flares or vents to safe location are appropriate for large gas volumes passing for a short time period.

**(f) Catalytic oxidation**

Available ammonia is oxidised at 150–250°C over a precious metal catalyst, forming nitrogen and water, according to the following reaction:



A support fuel may need to be burned to maintain the required reaction temperature. Periodic disposal of the catalyst is required. Undesirable species such as catalyst poisons and particulates should be avoided in the gas stream to be treated. The catalyst is now commercially available, but as yet (1998) there are no full-scale installations.

**2.4 Manufacture of fertilisers****2.4.1 Introduction**

The fertiliser manufacturing industry can be considered to be a mature industry. Owing to a variety of economic/financial pressures, the industry has undergone dramatic restructuring in

the last 30 years. The major fertiliser manufacturing companies in the UK are now owned by European-wide concerns. This consolidation within the industry is a trend that seems likely to continue. The last significant investment in new plant within the fertiliser industry was approximately 10 years ago. Many plants in operation are in excess of 20 years old.

Products manufactured in the UK include ammonium nitrate, ammonium phosphate, NPK fertilisers and single superphosphates through a variety of different processes.

Some fertiliser products such as urea are not currently manufactured in the UK.

The quantity of NPK blended fertilisers is increasing, since this method involves mechanical mixing which is a relatively low-cost and simple technique.

A number of informative industry guides are available. These include a series of eight booklets published by the European Fertiliser Manufacturing Association entitled Best Available Techniques for Pollution Prevention and Control in the European Fertiliser Industry.

## 2.4.2 Manufacture of ammonium nitrate

### (a) General

Commercial processes for the manufacture of ammonium nitrate depend almost entirely on the neutralisation of nitric acid using ammonia. On some plants the ammonia may be supplied as a liquid that is normally vaporised using waste heat from the process.

Ammonium nitrate fertiliser plants typically produce a dry, free-flowing, solid product from a concentrated solution of ammonium nitrate.

There are many variations in the operating details of the plants producing ammonium nitrate in a dry, usable form by the neutralisation process. However, there are three steps that are common to most plants. These are as follows:

- neutralisation of ammonia with medium concentration (50–70%) nitric acid, forming ammonium nitrate solution and steam;
- evaporation of the ammonium nitrate solution; and
- conversion of the solution or melt to solid particles of a controlled size range with specific characteristics as required by the market.

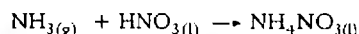
In some processes, the evaporation stage is eliminated as a separate step, by the reaction of preheated supplies of ammonia and high-concentration nitric acid. Consequently, there is very little water remaining for removal.

The following process description for the manufacture of ammonium nitrate details a typical neutralisation process with two-stage evaporation followed by prilling. A flowchart is shown in Figure 2.3.

### (b) Neutralisation

The strongly exothermic reaction of ammonia with nitric acid to form ammonium nitrate is typically performed between 145 and 185°C, and pressures up to 4.5 barg.

Ammonia, produced from either the evaporation of stored liquid ammonia or an associated ammonia plant, is superheated and passed to the reactor where it reacts with a heated supply of liquid, medium-concentration nitric acid. The nitric acid may be preheated by using steam or hot condensate from the ammonium nitrate process. This neutralisation typically forms a 75–85% solution of ammonium nitrate:



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 during the neutralisation. However, ammonium nitrate becomes less stable if the pH is below 4.5 and care must be taken that the bulk pH does not fall below this level. Effective control is essential.

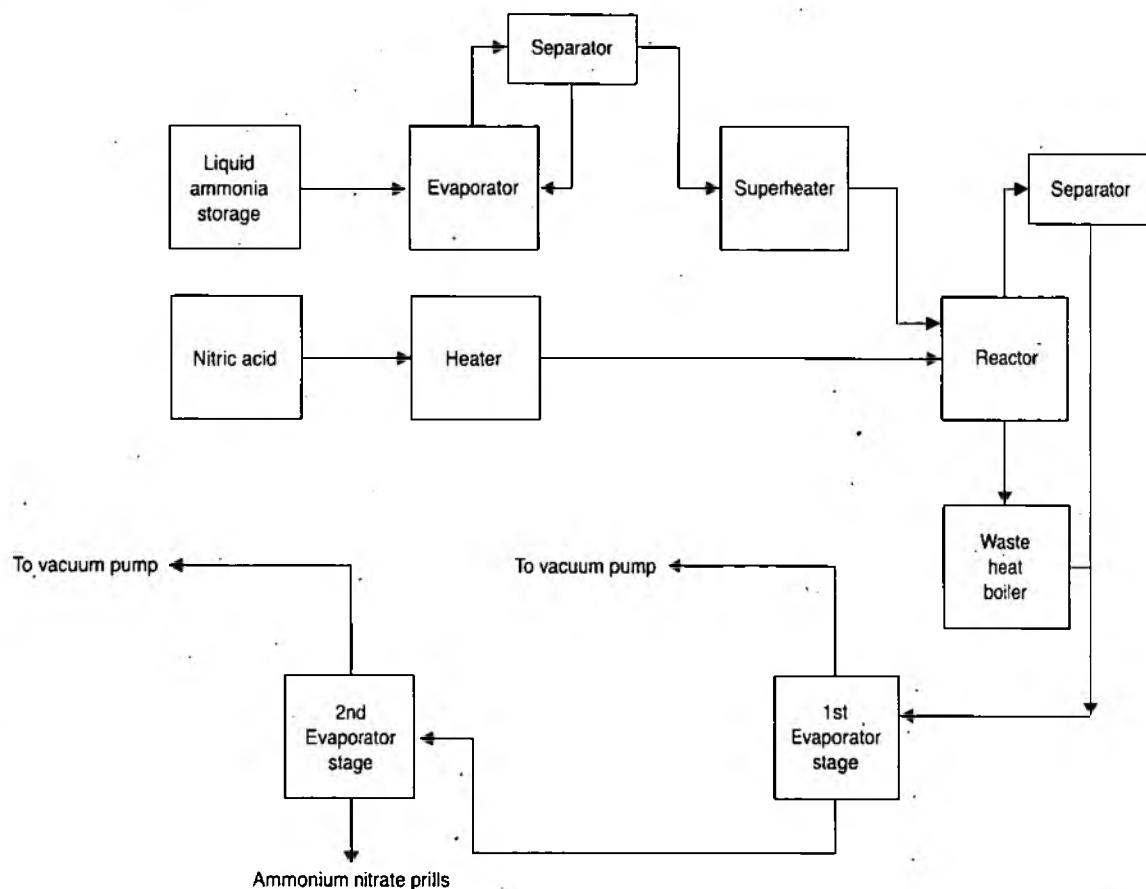
The neutralisation reaction may be carried out in either one or two reactors. When a single reactor is used the pH of the reaction mixture is typically controlled between 5.0 and 5.5. When two reactors are used the first stage is operated at a pH in the range 1 to 3 while alkaline conditions are maintained in the second reactor.

The use of two reactors results in reduced emissions of ammonia since most of the boil-off steam is generated in the first stage and most of the ammonia emission is in the second stage.

A typical single reactor consists of a reaction chamber followed by an overhead vapour liquid separator to disengage the ammonium nitrate solution from the steam. The system allows ammonium nitrate from the separator to be recycled to the inlet of the reactor. Nitric acid is added to the recycled solution via a sparge pipe in the inlet pipework of the reactor. Ammonia is injected in the base of the reactor and into the upward flow of solution using a sparge pipe. The reaction takes place releasing heat that generates steam and forces the solution up into the separator. From the separator, ammonium nitrate overflows to the next process: either a second reactor or the evaporation system, with some solution recycled.

The temperature of the neutralised solution can be controlled either by removal of the heat using the production of live steam in combination with a waste heat boiler installed on the reactor recirculation line, by addition of contaminated condensate from the evaporators, or alternatively by regulated addition of the reactants. Neutralisation at an elevated pressure will produce steam at a higher temperature (and 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 use of a scrubber employing acidified condensate, with the captured ammonia and ammonium nitrate

**Figure 2.3 Manufacture of ammonium nitrate**

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. In some processes it may be necessary to vent these from the neutraliser system at an appropriate point.

### (c) Evaporation

The procedures for evaporation of the neutralised solution vary depending on the water content of the reactants and on the evaporation temperature.

One - or two - stage evaporators, sometimes operating under vacuum, are in use in most plants. These units are thermally efficient and can be accurately controlled. The decomposition potential of ammonium nitrate requires that the second-stage unit be designed to retain only a small amount of the concentrated solution.

Ammonium nitrate solution from the reactor is passed to a vacuum evaporator system. The concentration of the ammonium nitrate solution obtained is dependent upon the number of evaporation stages, with a 95% concentration from single stage and a >99% concentration from two-stage evaporation.

Evaporation is always performed using steam, which can come from the ammonium nitrate process (neutraliser) or from a steam raising facility on the site.

The concentrated solution of ammonium nitrate must be kept at elevated temperatures to keep it as a liquid. Such a hot, concentrated solution of ammonium nitrate is called a melt.

Precautions are exercised to avoid contamination of the solution with any organic or other sensitising materials, since these will promote decomposition. Consequently the introduction of recycled streams is undertaken with great care.

### (d) Product Solidification

Ammonium nitrate is an important constituent of fertilisers and is required to be free-flowing with good storage properties. Ammonium nitrate is highly hygroscopic and cakes readily. The solid product should be protected from moisture and treated to minimise caking.

Various procedures, such as granulation, flaking and spraying, have been practised over the years to obtain ammonium nitrate particles or granules with size dependent upon the ultimate application.

There are two common methods for solidification, prilling and granulation.

#### Prilling

This final step in preparation of the product is often a

continuation of the evaporation procedure.

In the prilling process granules of fertiliser are formed by the solidification of droplets of fertiliser materials.

From the evaporation stage the concentrated solution of ammonium nitrate passes to the top of the prilling tower - a tall empty tower with an upward flow of air. Droplets are formed by the break-up of the liquid phase in a distributor head. As the droplets fall, they cool and solidify. 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. The air from the top of the tower contains ammonium nitrate fume and dust which requires abatement.

Some producers incorporate additives into the ammonium nitrate. 'CAN' is made by adding calcium carbonate or dolomite to the ammonium nitrate.

An internal additive of a magnesium compound is frequently added to the ammonium nitrate prior to prilling to act as an anti-caking and stabilising agent. A surface coating of a proprietary additive can sometimes be added to improve handling properties.

After the prills fall down the prilling tower they must be cooled further. This can be achieved by the use of a fluidised-bed cooler. The cooled prills are screened to remove small amounts of oversize and fines, which are then either recycled to the process or sold separately.

### Granulation

'Granulation' refers to techniques using processes such as agglomeration, accretion, or crushing to make a granular fertiliser. Typical granulators include rotary pans and fluidised beds.

Early plants use the prilling process, but from about 1973 some plants were built to produce a granular form of ammonium nitrate. The granulation process enables the production of granules of any reasonable size with decreased pollution problems compared to prilling due to the much smaller volumes of air handled.

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. Concentrated ammonium nitrate solution is sprayed onto a cascade of granules falling from specially designed flights. The granule size is built up mainly in successive onion-skin-type layers to produce well-rounded granules. After screening, the granules are further cooled and then can be coated with a surface conditioner if required.

In another process, the granular product is formed by spraying liquid ammonium nitrate onto a fluidised bed of recycled material. Evaporation takes place and the size of granules is built up. The resulting granules are screened and those within the product size range are removed. Smaller granules are further recycled while oversize material is crushed before being added to the recycle stream.

### Cooling

Product from granulators and prill towers is normally cooled in rotary or fluidised-bed coolers.

#### (e) Potential release routes from the manufacture of ammonium nitrate

##### Releases to air

- Gaseous ammonia and nitric acid from storage (vents and pressure relief devices).
- Particulates and ammonia from the 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.

#### (f) Control of releases from ammonium nitrate production

##### Liquid effluent

Steam from the neutraliser can be used for heating the evaporators. Steam from the evaporators is either removed directly or by vacuum pumps.

There may be possibilities for integration of various other site operations to use the liquid effluent streams from the liquid ammonium nitrate and granular ammonium nitrate plants. For example, integration of these plants with nitric acid production can offer significant opportunities to reach low levels of liquid effluent from the liquid ammonium nitrate/granular ammonium nitrate production operations. Process condensate from liquid ammonium nitrate production contaminated with ammonium nitrate can sometimes be used in the absorption section of the nitric acid plant. The scrubber liquor from the granular ammonium nitrate plant air cleaning section can be recycled through the further evaporation stages on the granulation plant, which use part of the liquid ammonium nitrate plant stream.

Any condensed steam may be passed directly to either the main factory effluent treatment plant (ETP) or to a local recovery facility.

The main requirement is to reduce levels of ammoniacal

nitrogen in the final effluent. Contaminated steam may be purified either before or after condensation. There are several techniques that may be employed for the purification of steam. For purification of steam before condensation, these include<sup>(9)</sup>:

- droplet separation techniques
  - knitted mesh demister pads,
  - wave plate separators, and
  - fibre pad separators using, for example, PTFE fibres;
- scrubbing devices
  - packed columns,
  - venturi scrubbers, and
  - 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. Alternatively scrubbing with ammonium nitrate solution followed by suitable demisting may be employed.

For purification of steam after condensation, techniques include<sup>(10)</sup>:

- stripping with air or steam with the addition of alkali to liberate ionised ammonia if required;
- ion exchange;
- distillation; and
- membrane separation processes.

The choice of technique will depend upon whether nitrate removal is required and this will depend upon the receiving water. Recovered ammonia may be re-used in the main ammonium nitrate process.

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 then strips the ammonium compounds from the condensate. The cleaned condensate is the bottom product from the column and forms the liquid final effluent from the process. It contains less than 50 ppm of the ammonium compounds; achieved levels in the range 5–10 ppm have been reported. The top product, which is steam containing 10–12% of ammonium compounds, 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 from the ETP corresponds to the water that is entering with the nitric acid.

Aqueous wastes may contain ammonia and nitric acid as well as particulate matter. This effluent produced by the fertiliser manufacturing processes may be acidic or alkali and may need to be neutralised.

### Dust pollution

Most of the pollution on an ammonium nitrate plant is derived from the dust and vapour that arise from prill towers or granulators.

The ammonium nitrate dust in the gas stream is a very fine (sub-micron) particulate fume (droplets and vapour) that, at concentrations above 15 mg/m<sup>3</sup>, becomes visible in the atmospheric discharge as a persistent blue haze after dispersion in the steam plume. This may be removed by irrigated candle filters (with candles incorporating fine glass fibre) with a cost representing a significant proportion of the total plant cost.

A candle filter installation that is specified to handle all of the prill tower exhaust gas is very large and expensive; for example, the gas flowrate associated with a 1700 tpd plant is about 500,000 m<sup>3</sup>/h and the cost of the pollution control plant is reported to be about £6 million. This includes the installation of cyclones on the fluidised bed.

The repacking of the candles is an expensive exercise costing many thousands of pounds.

Acidic solution at a pH of about 2 is circulated around the filters until it reaches a 40% ammonium nitrate solution. This can then be mixed with off-specification ammonium nitrate from the prilling process to give a 60% solution, neutralised using ammonia and then recycled to the neutralisation reactor. Pumps must not be allowed to become dead-headed as they could explode.

Mesh filters may be employed upstream of the candle filters to remove particulates. The mesh filter is washed with 40% ammonium nitrate in full solution acidified with nitric acid to pH 2. Under ambient conditions at this concentration, ammonium nitrate is stable.

Some designs of prill tower use an internal shroud fitted around the spray head to collect the finest fume generated from the spray process. Air extracted from within this shroud contains dust concentrations of 200–400 mg/m<sup>3</sup> whereas that from outside the shroud is typically 50–60 mg/m<sup>3</sup>. High-efficiency collectors for the dustier stream can be sized for a smaller flow than for the same process without a shroud, typically a candle filter.

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. This 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. Devices include candle filters, venturi scrubbers and cyclones. Candle filters are not suitable for control of dust pollution where either calcium ammonium nitrate or insoluble materials are added to the ammonium nitrate. This is because insoluble compounds rapidly foul the surface of the filter.

Techniques employed for cleaning air from prill towers and granulators may also be employed on coolers.

Air cleaned in a dry system may be re-used as secondary air to the dryer after de-dusting.

### ***Ammonium nitrate fume abatement***

The most effective technique for the abatement of ammonium nitrate fume is the use of irrigated candle filters, since conventional scrubbers are less efficient for removal of particulates  $<1\ \mu\text{m}$ .

The dust-laden airflow also entrains ammonium nitrate droplets/vapour and ammonia vapour, and so the filters are irrigated with an acidified solution to remove the dust and ammonia vapours.

The acidic solution is circulated around the filters until it reaches a 40% ammonium nitrate solution. It can be mixed with ammonium nitrate waste from the prilling process to give a 60% solution, neutralised using ammonia and then recycled to the neutralisation reactor.

A mesh filter can be used upstream of the candle filters, which is washed with a nitric acid solution to maintain acid conditions. In these cases the candle filters are irrigated with water rather than acid solution.

The choice of the fibre in the candle filter is very important. Organic materials of construction should only be used on ammonium nitrate plant after a detailed hazard study has established the safety of the application. Glass fibre is typically used but requires tight pH control since it is attacked by both acid and ammonia. Ammoniacal conditions lead to etching while acid causes a breakdown of the sodium silicate bond. Typically candle filters have a limited life of 3–5 years.

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.

### ***Storage and handling of ammonium nitrate solution***

Following manufacture, the liquid ammonium nitrate may be pumped into storage tanks. The temperature in the tank is maintained at a level to keep the ammonium nitrate in the liquid phase. Heat is usually provided through use of an external heat exchanger through which the ammonium nitrate is recirculated. Steam coils should not be used in ammonium nitrate storage to avoid any risk of use after solidification and potential detonation. Ammonia gas may be injected into the recirculating melt to maintain the ammonium nitrate at a stable pH and not allow it to decompose.

### ***Storage and handling of ammonium nitrate prills and granules***

Screened ammonium nitrate is conveyed/elevated into storage facilities. Fugitive dust emission should be minimised during transportation and bagging of the product. Prills and granules are generally dust-free.

## **2.4.3 Manufacture of ammonium phosphate**

Ammonium phosphate is produced by contacting phosphoric acid (50–55%  $\text{P}_2\text{O}_5$ ) with ammonia in a reactor. The exothermic nature of the reaction requires diluent water or contaminated condensate to be added to control the reactor temperature.

The ammonia, acid and diluent are mixed in the reactor and the resulting slurry is passed along a short length of pipe to the granulator. Sulphuric acid can also be added depending upon the required formulation of the final product fertiliser.

## **2.4.4 Manufacture of NPK fertilisers**

### **(a) General**

The basic plant nutrients found in chemical fertilisers are nitrogen (N), phosphorus (P) stated as phosphorus pentoxide, and potassium (K) as potassium oxide. Typical sources of these constituents are ammonium nitrate, ammonium phosphate and potassium chloride respectively.

The product name is normally followed by three numbers that indicate the relative percentages of N,  $\text{P}_2\text{O}_5$ , and  $\text{K}_2\text{O}$ . The typical content of nutrients normally totals between 40 and 60%.

The process for compound or complex fertilisers such as NPK is more difficult to define as there is an infinite number of N/P/K ratios and the processes applied in their production are numerous.

Some of these processes are not carried out in this country for a variety of economic/financial reasons. One such process is the nitric acid route or nitrophosphate process. This process aims to produce nitrate-containing straight and compound fertilisers starting from rock phosphate and using all the nutrient components in an integrated process without solid wastes and with minimal gaseous and liquid emissions.

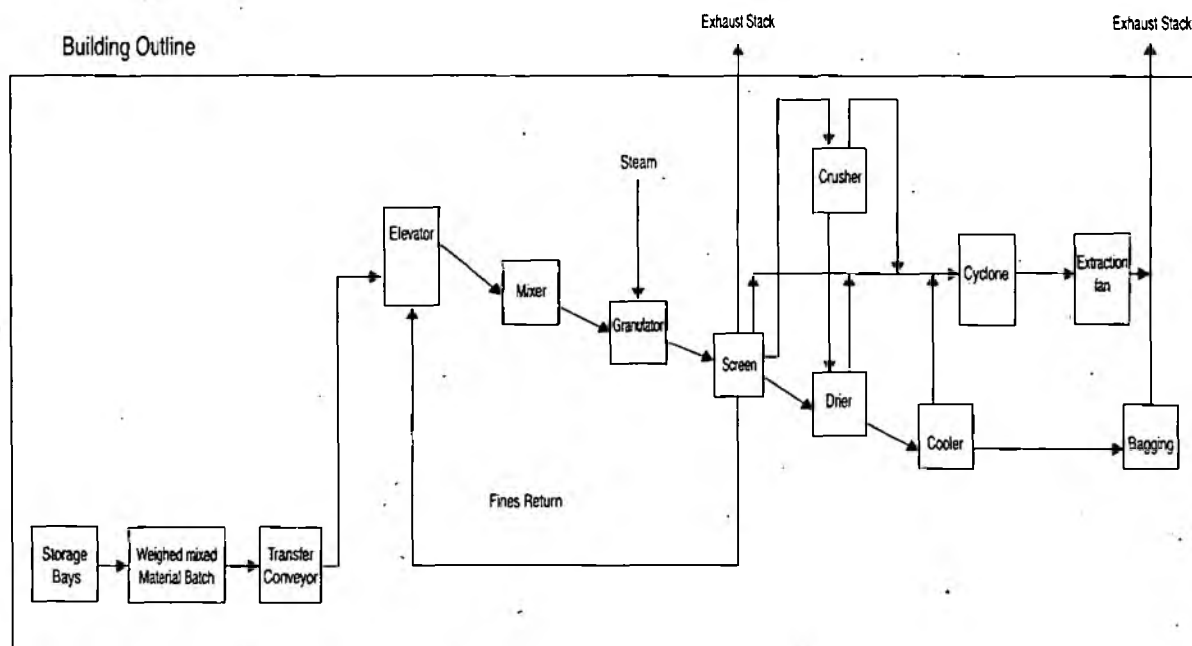
Other processes include the mixed-acid process, the ammonium phosphate/ammonium nitrate route, and the mechanical blending of single or multi-nutrient components.

Processes covered in this Note are those operated in the UK and include the ammonium phosphate/ammonium nitrate route, and the mechanical blending of single or multi-nutrient components.

The preferred form of a solid fertiliser is a free-flowing, dust-free product. Compound fertilisers are produced in two forms, either as granular or as blended product.

### **(b) Difference between granulated and blended products**

A uniform compound fertiliser is manufactured by mixing solid and/or liquid raw materials, some of which may react, to produce a granular product. The following feed materials may be used in the manufacture of NPK compound fertilisers:

**Figure 2.4 Typical granulation process**

ammonium nitrate, ammonium phosphate, ammonium sulphate, urea, single superphosphate, triple superphosphate, potassium chloride and potassium sulphate. Each granule contains the N, P, K plant nutrients at levels close to and averaging the declared values for the grade.

A blended compound fertiliser is manufactured by mixing solid raw materials. Blends do not necessarily consist of mixtures of straight fertilisers or single compounds. A blend of two or three uniform compounded fertilisers is still a blended fertiliser. Blended fertilisers are made without involving any chemical reaction.

### (c) Granulation processes

The main chemical feeds for granulation can be produced on an adjacent plant, as often happens with ammonium nitrate, or bought in from other UK sites (eg ammonia) or imported from abroad (eg phosphoric acid and urea).

Granulation plants are normally housed within a large totally enclosed building to maintain dry conditions for the raw materials, the plant equipment and the bulk product. After the final product has been bagged, it can be stored outside ready for shipment. The flowchart of a typical process is shown in Figure 2.4.

Granulation plants fall into two main categories, these being 'water-balance-limited plants' and 'granulation-limited plants'. Granulated product may also be made by a third method known as compaction granulation.

#### Water-balance-limited process

In plants where this process is employed, there is much more water associated with the raw materials than is required to form the solution phase for granulation. These plants are sometimes called 'true granulation plants'.

A wide variety of raw materials may be used, generally depending upon the required fertiliser composition. The basic raw materials may include ammonium nitrate, phosphoric acid, potassium chloride, ammonia, potassium sulphate, superphosphate, secondary nutrients, micronutrients and filler.

Superheated ammonia is reacted with phosphoric acid in a pipe reactor. This exothermic reaction produces ammonium phosphate slurry. The temperature may be controlled by introduction of recycled scrubber solutions.

The ammonium phosphate slurry is then fed forward into a granulation reactor where it is reacted with ammonium nitrate.

The required solid raw materials are commonly added to the recycle stream, upstream of the granulator. They may also be introduced by mixing with the ammonium nitrate solution. These are metered into the process.

Solid raw materials, ie potassium chloride, and limestone filler are collected from storage, eg by front end loader, discharged into a hopper from which the materials are conveyed and then elevated into buffer storage bins.

Raw materials are fed at a controlled rate to the granulator, where they are mixed with ammonium nitrate solution and recycled solids (fines and crushed solids). Ammonium nitrate is added generally as a liquid/melt, forming the bulk of the liquid phase required for granulation.

The tumbling action of the material ensures the production of a homogeneous mix and aids the chemical reactions and granule growth. Product granules are spherical with typical diameters between 2 and 4 mm.

Wet granules from the granulator are discharged into a rotary co-current hot-air dryer. These can be as large as 30m long and 5m in diameter. The operation of the dryer is controlled

according to the inlet and outlet temperatures. Apart from the evaporation of any excess water, the drying process also strengthens the granules against breakdown during subsequent handling. Air leaving the dryer contains dust and some traces of ammonia and passes to a wet scrubber.

The material leaves the dryer at about 90°C, and is fed to vibrating screens. Oversized granules are crushed and then added, along with the undersized material, to the recycle stream.

The product is cooled to 40°C using air, after which the material is further screened to remove any fines formed by degradation in the cooler.

### *Granulation-limited process*

In this type of process the water associated with the raw materials is less than is required to form a sufficient solution phase for granulation and a subsidiary supply of water, typically steam, is necessary. These plants are sometimes labelled 'mixer granulation plants'. In certain plants the raw materials are all solids. In some cases no chemical reaction is involved.

Powdered materials are transferred by a combination of conveyor, elevator and screw feeder to a series of mild steel rotating drums, the first of which may be used as a premixer.

The granulation plant can be either a rotary drum, where steam or hot water is injected, or a high-speed paddle mixer, where hot water only is used.

The wet granules are transferred to a dryer that is typically a mild steel rotary drum fitted with lifters designed to drop all of the differently sized particles through a stream of hot air. High air velocities are avoided to prevent solids carry-over.

The processes downstream of the dryer are similar to the water-balance-limited process outlined above.

The granules from either the water-balance or granulation-limited processes are then coated with a suitable oil, followed by the application of a very fine coating agent, such as talcum powder, kaolin, or other suitable anti-caking agent, to enhance the storage and flow characteristics. Talc is more difficult to handle than clay and it therefore has to be aerated to enable free flow. These coating agents are all in the range 1–10 µm in size.

The coating is achieved by spraying the warm oil in the front section of the drum onto the rolling bed of the granules. This creates a thin film of oil around the 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 coating oil or bonding agent is also known as a dust suppressant.

The granulated product is then conveyed to the bagging section or the bulk storage area. Off-gases from the granulator and dust-laden airflows should be passed to the gas cleaning plant.

### **(d) Blending processes**

The blending process can be undertaken by either a batch or continuous process.

Blending processes are also carried out by companies not involved in mainstream fertiliser production. These companies are not encompassed by IPC Authorisations and therefore are not subject to the same discharge constraints since they do not use processes involving chemical reaction.

Blending involves the physical mixing of dry powders or granules. The individual fertiliser materials 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. It is sometimes necessary to coat and/or screen the blended material to ensure a uniform particle size distribution within any one mix.

Micronutrients may be added to blended fertilisers in either granular or powder form. It is common practice to add the micronutrient in powder form with a binding agent when the micronutrient carrier represents <5% of the total weight.

Incompatibility problems between certain raw materials may lead to changes in the physical properties of blends, in terms of both solubility and hygroscopic properties.

### *Batch process blending*

Raw materials are fed through a hopper into a mixer in which thorough mixing takes place for approximately five minutes before discharge. The mixed product is fed by conveying systems to the bagging section for packaging.

### *Continuous process blending*

Ideally suited to long production runs of a small number of formulations, continuous processing requires virtually no formal mixing to achieve consistent product analysis since the raw materials are metered from weigh hoppers by continuous weigh-feeders.

### *Liquid fertilisers*

These may be clear solutions or suspensions of fertiliser materials blended in water. They vary from single materials to complex mixtures of nutrients and trace elements. The only chemical reaction occurs in the production of diammonium phosphate suspension or solution by the neutralisation of monoammonium phosphate or phosphoric acid with dilute (18%) aqueous ammonia.

### **(f) Potential release routes from granulation/blending processes**

#### *Releases to air*

- Ammonia emissions and particulate emissions of ammonium nitrate, ammonium phosphate and potassium chloride from the granulator, the blender, the dryer, dust from the cooler and dust collection plant emissions.
- Fugitive dust emissions from the conveyors, screens and other solids handling equipment.



- Ammonium chloride and fluorides (from the phosphoric acid) from the granulation plant.

#### *Releases to water*

- Wash-down releases and scrubber liquors.

#### *Releases to land*

- None.

### **(g) Control of releases from the manufacture of NPK fertilisers**

#### *Sources of pollution on NPK fertiliser plants*

The main sources of pollution on a compound fertiliser plant are the ammonia and dust emissions from the granulator and the dryer, and dust from the cooler.

There can be traces of fluorides in the stack gases arising from the phosphoric acid.

There are also fugitive dust emissions from the conveyors, screens and other solids handling equipment.

Another potential source of pollution on NPK plants is the formation of a fine ammonium chloride.

#### *Effect of dust size on cleaning plant design*

An important parameter affecting the design and selection of suitable dust cleaning plant is the size and nature of the fume to be collected.

The particle size of dust in the exhaust gases from the granulator and the dryer is generally in the range 5 µm and above, with a little material between 3 and 5 µm in size.

The absence of small particles results in easy de-dusting in a low pressure drop (150 to 350 mm water gauge) device such as a wet cyclone.

#### *Comparison of wet scrubbing and dry collection cleaning plants*

The two main gas cleaning duties (ie cleaning of granulator and dryer gases) on a fertiliser plant require the use of wet scrubbing devices after primary treatment in cyclones.

This is because the gases contain water vapour and any condensation would seriously impair the operating effectiveness of bag filters or other types of dry cleaning equipment. Also, apart from the de-dusting duty, there is a requirement for ammonia and possibly fluoride absorption.

One problem associated with the use of wet scrubbers for all of the gas cleaning duties around the plant is that the plant water balance is affected. The bleed from the main scrubber can be returned to a pipe reactor but any surplus of liquor from the scrubber systems has to be either sold as a liquid fertiliser or disposed of 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 component of the running cost is the power required to overcome the gas-side pressure drop.

Table 2.4 illustrates the typical pressure drop and dust collection efficiency of several wet scrubbing devices used on fertiliser plants.

The scrubbing liquor used in the wet scrubbers may be ammonium phosphate or ammonium sulphophosphate solution. The pH of these solutions may be controlled by the addition of phosphoric and/or sulphuric acid.

**Table 2.4 Performance of wet scrubbers**

Type	Pressure drop	Dust collection efficiency (%)		
		1 m	5 m	10 m
	(mm WG)			
Simple void spray tower <sup>(a)</sup>	50	40	94	96
Medium pressure drop scrubber	150–350	90	97	99
Venturi scrubber <sup>(b)</sup>	600–1200	97	99.6	99.9

<sup>(a)</sup> 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.

<sup>(b)</sup> Venturi scrubbers operating at low pressure drops are available, in which case the expected performance is in the second category.

#### *General de-dusting*

For water balance reasons, the use of bag filters may be preferred for general de-dusting duties such as the ventilation of conveyors and the other solids handling equipment. Because of the relatively high dust loading the bag filter plant has to operate with a relatively low filtration velocity (<1 m/min) and a low pressure drop (75–100 mm WG). This results in extended 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 being collected is hygroscopic and therefore the filters have to be fitted with heaters. Air, heated with a steam coil to 100°C, can perform this duty. The heaters should be left running when the plant is shut down.

#### *Fertiliser plant scrubbing*

The main problem in a fertiliser plant scrubber is the practical

one of plugging. Fertiliser 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 fertiliser industry has used the Doyle impingement scrubber in which the contaminated gases are passed through an annular section formed by the insertion of a cone in the bottom of the downcomer duct. This allows the dusty gas to impinge at high velocity on to the surface of a bath of liquid. The scrubber liquor contains up to 40% of dissolved solids. Such a unit requires a pressure drop of 150–200 mm WG. The disadvantage for the granulator gas cleaning duty is in the gas having to pass through two units in series to ensure satisfactory dust removal. Furthermore the Doyle scrubber cannot be regarded as an effective absorption device. It has been found that when the Doyle scrubbers are operated under acidic conditions, i.e. with the addition of phosphoric acid, there was a 'steamy' plume and emissions of hydrogen fluoride. There was also a tendency for blockage to occur.

There are now scrubbers available in which the liquid gas contact is more efficient. This allows absorption and de-dusting.

### Airmix scrubber

The Airmix scrubber has been widely used in the industry. This is a self-induced spray-type device in which the gas and scrubbing liquid enter the bottom of the unit at high velocity. They are then decelerated in the diffuser section so that the liquid droplets tend to fall out of the gas stream to form a curtain of spray through which the gas stream passes and is scrubbed accordingly.

### Granivore

The cyclonic spray unit, in which the liquid is introduced through the sides of the scrubber, also relies on a vigorous scrubbing action in a dense spray for effective operation. The Granivore scrubber uses this principle. The location of spray nozzles across the gas stream should be 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. The particular advantage of this scrubber is that it simultaneously absorbs and de-dusts.

### Cyclones

Cyclones are generally employed as the main particulate abatement in the manufacture of chemical fertilisers. 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  $\mu\text{m}$

thereby making them suitable for the exhaust air from granulators, coolers and dryers. Smaller particles down to about 0.5  $\mu\text{m}$  can be separated where agglomeration occurs. High-efficiency cyclones are capable of removal efficiencies of the order of 90% for particles down to 5  $\mu\text{m}$ . After this, collection efficiency drops off appreciably. High-rate gas cyclones have a removal efficiency of about 90% for particle sizes down to about 20  $\mu\text{m}$ .

### 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°C, giving rise to a plume that is visible and steamy in appearance.

## 2.4.5 Manufacture of single superphosphate

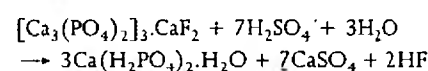
### (a) General

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. There are two types of these currently operating in the UK, the Broadfield den and the Maxwell den.

The operating principles are essentially the same. Both produce solid superphosphate in a powdery form using equipment that provides sufficient residence time for the SSP reaction to occur, although maturing of the product takes place for up to two weeks after this time.

### (b) Chemical reactions

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:



The calcium sulphate remains in the product and forms part of the fertiliser. SSP contains about 20% of phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) equivalent, and in the past it used to be sold as 0-20-0 product.

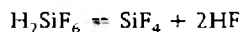
The chemical impact of acid on phosphate rock liberates large amounts of steam, which must be vented away from the working area. This contains rock dust, acid fumes and noxious gas, most of which originates from impurities in the rock. The dust consists of fine particulate material that becomes airborne before it can be retained by the acid.

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 ( $\text{H}_2\text{SiF}_6$ ).

Any excess silicon dissolves (in acid) to form silicic acid ( $\text{SiO}_2 \cdot \text{H}_2\text{O}$ ). Typical phosphate rock has about 8% silica ( $\text{SiO}_2$ )

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:



Both  $\text{SiF}_4$  and HF are gases at ambient temperatures and pressures and are collected by the den scrubbing system. The fluoride evolution varies between 10 and 50% of the fluoride in the rock, depending mainly on the concentration of the sulphuric acid. The fluoride emission increases at higher acid concentrations.

The  $\text{SiF}_4$  hydrolyses to form silica that potentially could present maintenance problems within the scrubbing system. Consequently, simple void spray towers and pigtail nozzles are preferred with once-through flow of scrubbing water.

During the curing process there are further fluorine 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.

#### (c) The Maxwell den

The shape of the Maxwell den may be likened to that of a motorcar tyre cover that slowly rotates in a vertical plane. In place of the rubber cover there is a cast-steel trough about 6 m in external diameter and 1.5 m in cross-sectional diameter. When in production the reactor contains 12 tonnes of solid.

The total residence time for the mixture to pass through the den is about three hours, and the typical output from a Maxwell den is about 3 tonnes per hour.

#### (d) The Broadfield den

The Broadfield den is essentially a horizontal tunnel, constructed from wood. The slurry of acid and rock moves through the den on a slowly moving slatted conveyor.

The residence time in the Broadfield den depends on the speed of the belt; typically it is about one hour. Broadfield dens can be sized to handle throughput of up to 10 tonnes/hour.

The solid material leaving the den is broken with a rotary cutter and transferred to storage piles where further curing takes place and time is allowed for the completion of the chemical reactions.

#### (e) Storage and maturing

The superphosphate from the den contains about 10% moisture. Material is then transferred to storage piles where further curing takes place. During this maturing stage the moisture content can reduce and the material can cake in the storage pile. It is dug out with a mechanical shovel and despatched in either bulk or packaged form. The SSP is both an

intermediate product used to make compound fertilisers and a horticultural fertiliser product. It is, therefore, not necessary to complete the curing process, that would occur over a ten-day to two-week period.

#### (f) Potential release routes from the manufacture of single superphosphates (SSP)

##### 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, mentioned above, and plant wash-down.
- Mercury from metallurgical sulphuric acid, present in the weak acid effluent, mentioned above, and plant wash-down.

##### Releases to land

- None.

#### 2.4.6 Control of releases from the manufacture of single superphosphate (SSP)

##### (a) General

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.

##### (b) Exhaust gas cleaning

Initial cleaning is achieved using one or more void spray towers arranged in series, operating with once-through scrubbing water, avoiding the possible build-up of solids that could occur through silica deposition.

A high-efficiency scrubber is needed for the second stage. A venturi scrubber with a pressure drop of 600 to 1000 mm WG 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 can be illustrated as in Table 2.5.

**Table 2.5 Emission from a Maxwell den**

	Inlet	Outlet
Sulphur dioxide, (mg/m <sup>3</sup> )	300	40
Sulphur trioxide, (mg/m <sup>3</sup> )	100	2
Fluorine compounds, (mg/m <sup>3</sup> )	90	1
Particulate matter, (mg/m <sup>3</sup> )	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 ingress 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. This can be prevented by ensuring adequate hooding around potential release points or by providing enhanced ventilation from a stand-by fan for use at start-up.

#### 2.4.7 Control of releases from the manufacture of fertilisers (general)

##### (a) Material handling systems

In the fertiliser manufacturing, granulation and blending plants, the most dusty areas are those surrounding the material handling systems.

When the material is in granular form, the generation of airborne dust is negligible and the storage areas are reasonably clean.

Where appropriate, the materials handling operations within a fertiliser manufacturing plant should be carried out using totally enclosed conveyors with enclosure of transfer points and other solids handling equipment.

##### (b) Material storage and reclamation

The storage bins into which dusty material is transferred by elevator or conveyor belt should be fitted with dust filter units on the air vents. When material is withdrawn from the storage bins, this should be done under controlled conditions using a totally enclosed feed device such as a belt weigh feeder, a vibratory feeder or a screw feeder.

##### (c) Conveyors

Much of the material transfer is carried out within the main building and therefore the material is not subjected to the effects of wind. This allows the use of many open belt type conveyors.

Dust escape can be avoided by using totally enclosed belt conveying systems. Such systems should be specified for new plant or retrofitted to existing plant on which there is a dust problem. A slight reduced pressure should be maintained within the conveying enclosures.

Totally enclosed forms of conveyors are available and include drag bar, screw, vibratory and pneumatic conveyors.

Material drops at conveyor transfer points should be kept to a minimum to reduce airborne dust and material degradation.

##### (d) Elevators

Elevators should normally be totally enclosed and fitted with an adjustable take-off point to serve as a dust extraction connection

to the main bag filter system. An 'anti-run-back' device should be fitted as standard practice. Elevator chain speeds should be carefully selected considering the size and nature of the material being handled. This will minimise airborne dust and degradation at the feed and discharge sections.

The capacity of the bag filter units for the general de-dusting of the conveyors, elevators and the transfer points should be designed to give a slight reduced pressure within the area being de-dusted.

##### (e) Screens

Through the nature of their operation, vibrating screens create air/material movement and cause fine dust to be formed, which could give rise to dust pollution of the area surrounding equipment.

Where regular cleaning of screens is not required, total enclosure should be employed.

##### (f) Bag packing area

Bags can split when being filled, transported or loaded on to lorries. When such spillage occurs it should be cleared up promptly otherwise dusty emissions and fugitive dust may result, with a possible hazard occurring due to the hygroscopic nature of the fertiliser material.

##### (g) Maintenance

Resistant materials of construction and a high standard of maintenance are required to prevent the effects of erosion and corrosion resulting in fugitive losses.

## 2.5 Hydrogen cyanide

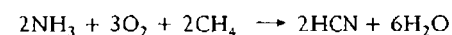
### 2.5.1 Introduction

Hydrogen cyanide in the UK is produced directly and also sourced as a by-product from acrylonitrile production. It is widely used in the form of sodium cyanide for a diverse range of applications. Cyanide solutions are widely used throughout the metal finishing industry (see Section 2.9 on cadmium for a discussion of techniques applicable to the treatment of cyanide plating solutions).

### 2.5.2 Processes for the manufacture of hydrogen cyanide

#### (a) Andrussow process

This is the only process producing first-intent hydrogen cyanide currently operated in the UK. The feedstock is a gaseous mixture of ammonia, air and natural gas which is passed over a platinum/rhodium catalyst at 1100°C to give hydrogen cyanide, water and a significant quantity of impurities. The required reaction is:



Variations of this process use oxygen-enriched air or simply oxygen.

The reaction is exothermic and heat is recovered as process steam and preheated boiler feed water.

The work-up consists of a series of process steps:

- Absorption of water and unreacted ammonia into ammonium sulphate/sulphuric acid solution, producing ammonium sulphate solution.
- Absorption into chilled water to remove the hydrogen cyanide from the gas stream. The tail gases pass to a burner for heat recovery of the calorific value of the stream.
- Stripping and distillation of the hydrogen cyanide solution to give pure product. Heat can be recovered from the still bottoms.

During start-up, feed gas passes to a diverter stack until correct conditions have been established to allow the gauze to be lit safely.

Distillation and stripping vents are fitted with refrigerated guard condensers to maximise recovery of hydrogen cyanide. Stabilisers (usually sulphur dioxide, phosphoric acid or acetic acid) are added to condensed hydrogen cyanide and the vapour spaces to prevent polymerisation.

The efficiency of the main reaction falls as the catalyst becomes exhausted.

#### (b) Potential release routes from the Andrusow process

##### *Releases to air*

- Methane, ammonia, hydrogen cyanide, carbon monoxide and carbon dioxide, which should be used as fuel in the tail gas burner.
- Methane and ammonia during start-up conditions, and hydrogen cyanide from plant ventilation systems.

##### *Releases to water*

- Ammonium sulphate liquor, various cyanide-containing liquors from the process and washing liquors containing sulphuric and phosphoric acid.
- Cyanide containing liquors are treated under pH control with hypochlorite to destroy the cyanide.

##### *Releases to land*

- There are no planned releases to land. Spent catalyst should be returned to the supplier for recovery.

#### (c) Degussa (BMA) process

In this process ammonia is reacted directly with natural gas, at elevated temperature and in a tube reactor, in the presence of a platinum catalyst.

The process, which is endothermic, obtains good conversion

without the impurities formed in other processes. However, the advantages of this are countered by the criticality of process conditions to the prevention of reactor damage. The economics of the process are likely to depend on the operator having a use for the co-produced hydrogen.

This process is currently not operated in the UK.

#### (d) Potential release routes from the Degussa (BMA) process

##### *Releases to air, water and land*

- The releases are similar to those from other processes producing hydrogen cyanide.

#### (e) BP Sohio process for acrylonitrile production

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 impurities.

The work-up consists of a series of absorption, stripping and distillation techniques to yield acrylonitrile and hydrogen cyanide.

The hydrogen cyanide is generally sold to a third party, but can be burnt in a boiler for safety reasons if the onset of polymerisation is detected or if no market exists. This process is covered more fully in IPC Guidance Note S2 4.01<sup>(20)</sup>.

### 2.5.3 Processes using hydrogen cyanide

#### (a) Manufacture of sodium and potassium cyanides

These processes can be carried out batchwise or continuously. In each case hydrogen cyanide is added to a solution of either sodium or potassium hydroxide. Careful control of reaction conditions and parameters is required to prevent the formation of either by-products, such as sodium formate, or hydrogen cyanide in the product solution.

Depending upon the source of the hydrogen cyanide, further processing of the liquor may be required to remove the respective carbonates and bicarbonates that can be present in the solution. If carried out this purification stage results in the production of a calcium carbonate/bicarbonate-based waste slurry.

Sodium and potassium cyanides in the solid form are produced by evaporating the above solutions and filtering a product slurry. The evaporator condensate can contain ammonia and hydrogen cyanide and so passes to effluent treatment. The solid product is removed from the slurry using centrifuges with the filtrate being returned to the evaporator.

The product is dried and can be compacted in a press to produce dustfree lumps. Granular material can be produced by coarse milling and screening of the lumps, any rejects from the screening process are recycled to the press. The dryer vent is scrubbed and any cyanide containing liquor returned to the process.

Local area extraction systems to remove dusts from the workplace contain cyanide-contaminated material, which should be recovered where possible.

**(b) Potential release routes from the manufacture of sodium and potassium cyanides**

*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, eg damaged packaging, filter media, etc. Wherever possible, items are washed with water to decontaminate and the resultant liquor treated as a release to water.

**(c) Manufacture of acetone cyanohydrin**

Acetone cyanohydrin is an intermediate in the production of methyl methacrylate and methacrylic acid (see IPC Guidance Note S2 4.01<sup>(a)</sup>). The majority of the acetone cyanohydrin is produced and consumed on the same site. Other routes to methyl methacrylate not involving the use of hydrogen cyanide are also in commercial use.

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.

**(d) Potential release routes from the manufacture of acetone cyanohydrin**

*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.

**(e) Manufacture of cyanogen chloride**

Cyanogen chloride can be manufactured on a continuous or batch basis. It is used as an intermediate for other chemicals (eg diphenylguanidine) and usually generated as required. For ease of processing, hydrogen cyanide feed is often generated in situ by the action of an inorganic acid on a solution of sodium cyanide. The hydrogen cyanide is generated as an aqueous solution. Chlorine gas is added under controlled conditions, generating cyanogen chloride gas, which is passed into the next reaction stage. The rate of cyanogen chloride evolution is controlled by the chlorine addition rate.

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 should vent to a total containment system.

**(f) Potential release routes from the manufacture of cyanogen chloride**

*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 Sections 3.4.3 and 3.4.4

*Releases to land*

- There are no planned releases to land.

**(g) Manufacture of other hydrogen cyanide derivatives**

Acidified sodium cyanide can be used as a source of hydrogen cyanide, or hydrogen cyanide can be used directly, in the manufacture of a range of chelating agents, cyano-pigments, cyano-organic chemicals or intermediates for a range of organic chemicals.

Most operations fitting in this category are batch operations. Potential releases are dependent on the specific processes.

**(h) Potential release routes from the manufacture of other hydrogen cyanide derivatives*****Releases to air***

- Hydrogen cyanide and volatile organic compounds from process vents, scrubber vents and ventilation systems.

***Releases to water***

- Cyanide, dissolved organic solvent, suspended solid organics and effluent treatment chemicals.
- Any cyanide containing liquors are treated to destroy cyanide by one of the methods indicated in Sections 3.4.3 and 3.4.4.

***Releases to land***

- Spent non-recyclable catalysts, effluent sludges, distillation residues and floor sweepings.

**2.5.4 Control of releases of hydrogen cyanide****(a) Storage and transportation**

Storage systems for hydrogen cyanide, which is classified as highly flammable, may be fitted with a water deluge system in case of fire. Any such fire water should be collected and treated before disposal.

To prevent polymer build-up in hydrogen cyanide systems, equipment (pipework, rail cars, etc) is routinely treated with dilute phosphoric acid. These washings should generally be retained for re-use but eventually they become exhausted and require treatment 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<sup>(1)</sup> (issued 1993) covers the storage and handling of hydrogen cyanide.

Sites storing 5 tonnes or more of hydrogen cyanide will also be regulated by the CIMAH<sup>(2)</sup> regulations, and a full safety case should already exist.

**(b) Use and handling of hydrogen cyanide**

Notwithstanding the Code of Practice of 1993, the following provides guidance to Inspectors on the techniques likely to be encountered within plants using and handling hydrogen cyanide.

Hydrogen cyanide is a highly flammable liquid and can polymerize in the presence of heat, alkali and moisture. At concentrations between 3 and 90%, autocatalytic, exothermic reactions 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 are 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°C. At temperatures above +5°C the vapour is above the upper explosive limit. The normal storage temperature is +1°C 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 could exist in head spaces and so polymer can build up in strategic areas (eg condensers). Most plants have systems for adding stabiliser to areas at risk, or 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 to either storage or process with an inert gas (usually nitrogen) and the lines washed with dilute phosphoric acid (or other stabiliser), which should be retained for reuse wherever possible.

Inventories should be kept as low as reasonably practicable without causing operational problems. Storage tanks should be segregated from other chemicals by means of a dedicated bunding arrangement.

In all known cases, strict procedures exist for the transport of hydrogen cyanide.

Stainless steel is the preferred material of construction. Pipe work should be continuously welded wherever possible and indirect drive or canned motor pumps should be used.

**(c) Gaseous effluent**

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 or incineration.

Most processes involving hydrogen cyanide that generate particles require very low emission levels (eg sodium cyanide manufacture). Because of this, it is unlikely that electrostatic precipitation or dust suppression will be suitable.

**(d) Liquid effluent**

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.

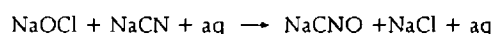
There are several chemical oxidation processes for treating

cyanides in water. The main methods currently in use are given below:

- excess alkali followed by sodium hypochlorite;
- hydrogen peroxide; and
- formaldehyde.

### *Sodium hypochlorite treatment*

The cyanide is oxidised to the cyanate by sodium hypochlorite at pH more than 10. The reaction is as follows:



It is imperative that pH is maintained above 10, otherwise cyanogen chloride and hydrogen cyanide may be formed.

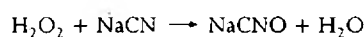
The reaction is rapid and the cyanate cannot readily be reduced back to cyanide. Cyanate is readily biodegradable.

This system lends itself to automatic control as the end-point can be checked 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. Therefore the final effluent should be continuously monitored for cyanide, chlorine and pH.

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.

### *Hydrogen peroxide treatment*

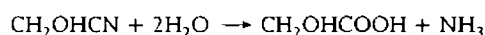
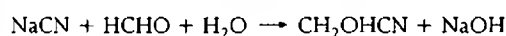
Hydrogen peroxide can be used to oxidise cyanide at pH ~9 to cyanate according to the following reaction:



Hydrogen peroxide is more expensive than hypochlorite but it is easier to control and cannot release chlorine. For this reason, it is often favoured by batch manufacturers who generally deal with smaller effluent volumes but where the cyanide content of the unreacted effluent can be highly variable.

### *Formaldehyde treatment*

At pH 8–14 formaldehyde oxidises cyanide to the cyanohydrin, which in turn slowly hydrolyses in water to ammonia as given in the following equations:



The process has the disadvantages that ammonia is formed, which can present an odour problem, and excess formaldehyde can be present. However, all other products are easily biodegradable and this 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.

### *Other methods*

Alternative methods can be used depending upon a number of factors including volume and composition of the waste. These methods include the following:

- ion exchange;
- enzyme degradation;
- biological treatment (in conjunction with other wastes); and
- high-temperature incineration (high concentrations only).

## **2.6 Hydrogen sulphide**

### **2.6.1 Introduction**

Hydrogen sulphide manufacture is not described. It is obtained almost exclusively in the UK as a by-product of carbon disulphide manufacture. Details of this process and any associated abatement equipment is given in IPGN S2 4.01<sup>(10)</sup>. Hydrogen sulphide is released from a wide range of inorganic and organic chemical processes authorised under this sector.

### **2.6.2 Manufacture of sodium sulphides**

#### **(a) Processes**

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 solution); excess-sodium-hydroxide produces sodium-sulphide solution.

NaHS solution is usually used without further treatment (other than dilution), whereas sodium sulphide solution may be processed further to give solid sodium sulphide.

This process is usually carried out at sites where substantial hydrogen sulphide is available as a by-product of another prime process (eg carbon disulphide manufacture). Any abatement therefore usually involves the abatement equipment associated with the prime process.

#### **(b) Potential release routes 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.

**2.6.3 Hydrolysis reactions****(a) Processes**

Hydrolysis of proteinaceous or other sulphur-containing organic compounds is usually carried out batchwise using alkaline conditions. The hydrolysis causes breakage of the peptide linkages and other bonds, resulting in a release of ammonia and hydrogen sulphide with traces of mercaptans and disulphides.

The rate of evolution of ammonia and hydrogen sulphide is dependent upon process parameters. It is usual for operators to define the 'worst case' and demonstrate that abatement plant will operate to BATNEEC standards at this condition, without causing harm to the environment.

The hydrolysis is usually carried out in aqueous suspension at atmospheric pressure and elevated temperature. The ammonia release tends to be during hydrolysis, whereas hydrogen sulphide release tends to be during subsequent neutralisation.

The process can involve filtration to remove inert solids and precipitated salts, and evaporation to obtain a solution of the correct concentration. This solution can be further formulated to give the final product.

Processes exist where any condensate is treated and recycled to the process, leading to a nil release to water.

**(b) Potential release routes from hydrolysis reactions****Releases to air**

- Ammonia, hydrogen sulphide with trace mercaptans and disulphides. Abatement can be by absorption using a wet scrubber or by tail gas incineration.

**Releases to water**

- There are no planned releases to water as given in the above section.

**Release to land**

- Filter cake containing inerts and precipitated salts, which are disposed to landfill.

**2.6.4 Viscose processes****(a) 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 dewatered using presses to form sodium alkali cellulose – the sodium hydroxide that is removed is recycled back into the process.

The alkali cellulose is then oxidised by air permeation to reduce the cellulose polymer chain lengths in order to achieve 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 to atmosphere.

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. Filtration of the solution is carried out to remove inorganic particles and any undissolved wood pulp. Prior to extrusion (spinning) the viscose is deaerated.

This viscose solution is then 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. 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 filaments are then collected together and stretched to align the cellulose molecules in the filaments.

At this point the filaments may be processed as a continuous tow or cut into staple fibres. In either case, the fibre is passed through a number of washing 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.

**(b) Manufacture of cellophane**

Xanthate solution is produced as described in Section 2.6.4(a) 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 changes 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/monopropylene glycol. The film is driven over a series of heated rollers in an oven, after which it is cut to size and supplied as a permeable uncoated variety. Permeable and semipermeable grades are also manufactured, and this is achieved by:

- incorporating an anchoring agent into the last bath of the wet process; and

- applying a coating to the dried film from a solvent-based or aqueous solution, the solvent being evaporated and subsequently recovered.

### (c) Manufacture of closures

Viscose, after ripening and conditioning to the correct viscosity, is extruded as a tube into a bath of ammonium sulphate. This operation gels the viscose. Ammonium sulphate is also pumped through the centre of the tube to sustain a cylinder during manufacture. The tubing is then conveyed through a series of baths. In the first bath cellulose xanthate is regenerated by reaction with sulphuric acid. This results in the generation of hydrogen sulphide, carbon disulphide and other sulphur compounds. Excess acid is then removed by passage through water, and dilute caustic baths. Residual sulphur is treated in a bath with hot sodium hydroxide and sodium sulphide. The next baths provide further washes to remove excess desulphurisation solution and at the end of the machine the tubing passes through a preservative solution appropriate to the intended use.

### (d) Manufacture of casing paper

Wood pulp is shredded and mixed with sodium hydroxide and carbon disulphide. This produces a uniformly xanthated crumb, which is dissolved to produce a homogeneous viscose solution. The casing is produced, when a dried paper web is fed through a bath of the viscose solution. This is dried before passing through an acid bath where cellulose is regenerated. The paper then passes through a wash section and acid press before passing to a final drying stage. Hydrogen sulphide and carbon disulphide are emitted from the acid regeneration operation and from the neutralisation operation.

### (e) Manufacture of sponge

Viscose sponge is no longer manufactured in the UK.

### (f) Potential release routes 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, carbon or biological filters may be considered.
- Amine, caustic scrubbing or other systems may be appropriate for particular releases.

#### Releases to water

- Liquid effluents will originate from scrubbing systems, process wastes and from routine cleaning of equipment. The effluents may contain carbon disulphide, hydrogen sulphide, mercaptans or other organic sulphur compounds.

- Effluents are likely to require primary and secondary treatment prior to discharge to the environment.
- Spent scrubber liquors can be treated with hypochlorite to form inert chlorates of sulphur. The use of hypochlorite or other easily handled oxidant (such as hydrogen peroxide or ozone) should be considered for the elimination of odours in effluent.

#### Releases to land

- Wastes intended for disposal to land are likely to contain organic sulphur compounds. Operators should ensure that these compounds are removed prior to the landfill of wastes or that the wastes are suitably contained to prevent the release of the sulphur component.
- Releases to land may include spent consumables from the process such as drums, sacks and rags. These may be contaminated with sulphur compounds and therefore generate odours.

## 2.6.5 Control of releases of hydrogen sulphide

### (a) Use and handling of hydrogen sulphide

Hydrogen sulphide is highly flammable and toxic, with a characteristic smell of rotten eggs at low concentrations. (Note. 50% of the population can identify the smell at 1 mg/m<sup>3</sup>. At higher (toxic) concentrations or after prolonged exposure, the smell cannot be detected, making the use of continuous monitors essential.

Indoor storage areas should be isolated and well ventilated. Hydrogen sulphide is stored under pressure (usually at 25 barg). 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. If water or water vapour is 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 efficient seal systems used (eg close-coupled pumps, flushed double seals).

Sites storing 5 tonnes or more of hydrogen sulphide will also be regulated by the CIMAH<sup>23</sup> regulations and a full safety case should already exist.

### (b) Gaseous abatement techniques

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 readily used within the inorganic chemical industry to remove hydrogen sulphide from vent streams. The pH must be carefully controlled since the removal relies upon an equilibrium reaction.

Alternative forms of destruction used include incineration, absorption into water, or other neutralising agent, or low-vapour-pressure oil according to the nature of the contaminants to be removed. Hydrogen sulphide and mercaptans are often found to be released in conjunction with organic species, which may determine the choice of technique to be used VOC removal techniques, etc.

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

New 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 can be used.

Most processes involving hydrogen sulphide that generate particles require very low emission levels. Because of this, it is unlikely that electrostatic precipitation or dust suppression will be suitable.

Waste streams rich in hydrogen sulphide can be passed through sulphur recovery units for conversion to elemental sulphur. Refer to "sulphur recovery" in Section 2.6.5(c) for details.

### (c) Sulphur recovery

New sulphur recovery plants should use enhanced techniques such as super Claus. Tail gas treatments such as flue gas desulphurisation, or SCOT process should be considered where appropriate.

There are several recovery techniques currently employed in other industries. Examples include:

- mono- and diethanolamine processes;
- hot carbonate process;
- sulfinol process;
- alkazid process;
- liquid redox processes Stretford process; and
- Claus sulphur recovery.

Many developments are currently ongoing to develop improved sulphur recovery systems.

#### *Mono and diethanolamine processes*

The amine compounds react with hydrogen sulphide and carbon dioxide to form inert compounds.

The amine absorbent passes counter-current to the sour gas in a packed column: sweetened gas passes for further treatment. 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. MDEA-based amine systems have a good

absorption efficiency and can be tailored to suit particular waste streams.

#### *Hot carbonate process*

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

#### *Sulfinol process*

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

#### *Alkazid process*

The alkazid process is a cyclic heat regenerative type. It uses a DiK solution containing the potassium salt of N,N-diethylglycine or N,N-dimethylglycine. This 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*

A viable alternative to amine stripping followed by sulphur recovery in a Claus unit is direct sulphur recovery from weak hydrogen sulphide streams by liquid redox.

Liquid redox technologies oxidise hydrogen sulphide in a liquid solution by the action of a number of mild oxidising agents to produce sulphur and water. The oxidising agents usually contain vanadium (the Stretford process) or iron (the Ferrox process).

The Stretford process removes hydrogen sulphide from effluent gases. It is a continuous liquid purification system that converts hydrogen sulphide to elemental sulphur. The gas stream is first washed in an alkaline solution containing dissolved vanadates and anthraquinone disulphonic acids, fixing the hydrogen sulphide. The liquid from the washing stage then passes to a reaction tank, where virtually all the hydrogen sulphide is converted to elemental sulphur. The next stage, oxidation, separates the sulphur from the solution, which can then be returned to the washing stage. The sulphur is floated off as a froth for the final stage of recovery. The sulphur is usually recovered from the slurry in a molten form by decantation under pressure, frequently with prior filtration, and is obtained in a pure saleable form.

The vanadium-based Stretford process can achieve removal efficiencies of 99.9%. The process is tolerant to fluctuating flowrates.

However, the use of vanadium may have undesirable environmental implications. Other processes utilising non-toxic iron-based catalysts have been developed.

### *Claus sulphur recovery*

After absorption in an amine scrubber the hydrogen sulphide can be recovered and passed to a sulphur recovery unit for conversion to elemental sulphur.

The amine stream passes to a regenerator where heat is applied to drive off the hydrogen sulphide. The overheads are cooled, with condensate being recycled to the column, and the acid gas (greater than 90% hydrogen sulphide) is passed to the sulphur recovery unit. The lean amine stream is recycled to the scrubber.

A Claus sulphur recovery unit operating with "split" flow and three catalytic stages is described.

Part of the acid gas is burnt with air in a furnace to produce sulphur dioxide and water vapour. Further hydrogen sulphide then reacts with the sulphur dioxide to produce water vapour and elemental sulphur.

Both reactions occur in the combustion stage and sulphur is condensed and removed from the exit gases. Further acid gas is added in a reheater and the mixture is passed to the first catalytic stage, containing a fixed bed of bauxite, where the second reaction continues. The reaction is equilibrium-limited and overall conversion of hydrogen sulphide to sulphur depends upon the number of reacting and condensing stages. To achieve acceptable conversion, three stages are required, or two stages and tail gas clean-up.

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

Sulphur recovery plants should operate to a recovery efficiency of at least 98% during normal operation which will normally require three catalytic conversion stages with the final stage utilising a selective catalyst (eg super Claus process) or with further treatment of the tail gas (where residual sulphur dioxide is reduced to hydrogen sulphide, which can then be recycled to the amine scrubbers).

Notwithstanding this requirement, operators should demonstrate to the Inspector that they have, where appropriate, considered further abatement techniques to achieve the achievable release level. New plant should use enhanced sulphur recovery techniques.

Sulphur recovery units operate efficiently over a limited throughput range and operators should take this into account when designing their facilities.

New developments for Claus recovery systems include Bio-Claus, a process that biologically removes sulphur dioxide from incinerated Claus tail gas. Further detail on Claus sulphur recovery is given in IPCGN S2 1.10<sup>(23)</sup>.

### **(d) Liquid effluent**

#### *Treatment of sulphides*

Hydrogen sulphide or inorganic sulphides can be present in scrubber liquors, wash liquors, etc. All such sources should be identified and the liquors treated prior to disposal.

Several methods of treatment exist. The most appropriate is largely dependent upon the volumes to be treated as given below.

#### *Steam stripping*

Where large volumes of aqueous wastes containing hydrogen sulphide exist, live steam can be injected to strip out the hydrogen sulphide as a vapour. The hydrogen sulphide is then treated in abatement plant designed to handle large volumes as described earlier.

#### *Air oxidation*

Minor process vents and extraction systems are often scrubbed with sodium hydroxide. The resultant sodium sulphide is readily oxidised by allowing air to pass through the scrubber. The rate of oxidation can be improved by the addition of catalytic amounts of iron or vanadium salts.

#### *Chemical oxidation*

Aqueous streams containing sulphide can be readily treated continuously or batchwise by a range of oxidising agents. Owing to its price and availability, sodium hypochlorite is commonly used. In this case, hypochlorite addition needs to be controlled 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.

#### *Biological treatment*

Biological treatment of effluent containing sulphur compounds is possible, but is susceptible to shock load. Strict control of conditions is required to prevent formation of hydrogen sulphide, which because of its low odour threshold could lead to odour noticeable outside the boundary of the premises.

## **2.7 Phosphorus and its compounds**

### **2.7.1 Introduction**

Phosphorus has not been manufactured in the UK since the early 1970s and resumption of manufacture is unlikely for the foreseeable future.

In spite of the wide diversity of chemical reactions involving phosphorus and organic compounds, the methods for carrying out the processes and the equipment used are very similar.

The process steps proceed from storage and measuring of reactants (some of which may have been prepared in prior

reactions, possibly in the same vessel) to reaction with the phosphorus compound. In some reactions all the phosphorus compound aliquot can be added in one step; in others the rate of addition is restricted, in order, for example, to control temperature rise or gas evolution. The process is completed by neutralisation/clean-up/purification of the batch followed by storage and dispatch as either product or intermediate.

### 2.7.2 Phosphorus

Phosphorus is imported into the country in rail tankers, road tankers, ISO tankers and drums. The phosphorus is loaded as a liquid, solidifies in transit and is melted for unloading. The phosphorus is blanketed by water, nitrogen or a combination of both.

Different sources of phosphorus will have varying trace levels of arsenic, iron, antimony and organic impurities, which may affect the release to water from processes using phosphorus.

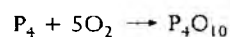
Trace organic impurities in the phosphorus can be rendered water-soluble. Subsequent washing of the phosphorus removes the organics. The washing can form part of the aqueous discharge to the site treatment plant.

Water used for blanketing phosphorus in storage (known as 'phossey water', due to the traces of phosphorus present) can form part of the aqueous discharge to the site treatment plant.

### 2.7.3 Phosphorus pentoxide

#### (a) Process description

Liquid white phosphorus is burnt with an excess of dry air in a combustion chamber to produce phosphorus pentoxide vapour.



The liquid phosphorus is atomised either by pressure or by air. Air for the process is dried by refrigeration.

The phosphorus pentoxide vapour is condensed as a solid by cooling, collected, and filled into containers and packages.

Traces of moisture in the phosphorus and air lead to the formation of lumps of polyphosphoric 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 treatment plant.

The off-gases comprising excess air and entrained phosphorus pentoxide pass to a scrubber where the phosphorus pentoxide is scrubbed out with dilute phosphoric acid. The gases leaving the scrubber are directed to air via a mist eliminator and stack. Droplets of phosphoric acid removed by the mist eliminator return to the scrubber. Surplus phosphoric acid from the scrubber is incorporated in phosphoric acid production. Trace phosphorus pentoxide, not removed by the mist eliminator, will be a minor component of the emissions to air. The trace phosphorus pentoxide will combine with moisture in the

atmosphere to form a fume of phosphoric acid droplets. Oxides of nitrogen may form in the combustion chamber and the efficiency of the scrubber and demister in removing these will need to be evaluated.

Variations to the process include:

- additional drying of combustion air with silica gel to lower dewpoints to reduce formation of polyphosphoric acid; and
- enrichment of combustion air with oxygen.

#### (b) Potential release routes from the manufacture of phosphorus pentoxide

##### Releases to air

- Small amounts of white phosphorus, as phosphorus pentoxide, from raw material delivery.
- Phosphorus pentoxide and phosphoric acid mist from scrubber and demister.
- Nitrogen oxides formed during combustion via scrubber and demister.
- Localised particulate from product handling and package filling.

##### Releases to water

- Blanket 'phossey' 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 is hydrolysed to phosphoric acid.

All releases to water are to a site treatment plant.

##### Releases to land

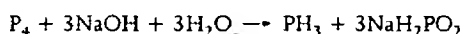
- Calcium phosphate and trace amounts of phosphorus from neutralisation of 'phossey' water and dilute phosphoric acid with calcium hydroxide.

### 2.7.4 Phosphine

Phosphine ( $PH_3$ ) can be manufactured by two routes:

- Reaction of red phosphorus with steam in the presence of an acid
 
$$2P_4 + 12H_2O \rightarrow 5PH_3 + 3H_3PO_4$$
- Electrolysis of white phosphorus in an aqueous electrolyte
 
$$P_4 + 12H^+ + 12e^- \rightarrow 4PH_3$$

Phosphine is also generated as a by-product by alkali catalysed disproportionation:



This route is operated for the production of sodium hypophosphite, or for the production of calcium hypophosphite using calcium hydroxide as the alkali.

#### (a) Acid catalysed route

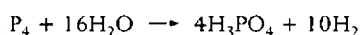
Phosphorus is fed continuously into the reaction vessel, which is maintained under an inert atmosphere by a nitrogen purge.

The phosphine reactor contains phosphoric acid. Steam is injected into the reactor and phosphine gas is continuously evolved. In order to prevent air ingress, which would be likely to cause an explosion, the process is operated at slightly positive pressures.

The phosphoric acid co-product is withdrawn at intervals.

The unreacted phosphorus in the phosphine leaving the reactor is condensed and recycled as liquid.

The gaseous phosphine product contains about 1–2% of hydrogen formed by oxidation of some phosphorus with steam



and 3–5% nitrogen from blanketing of the reactor.

The phosphine gas product is stored in a water-sealed gas holder.

Pressure relief will result in phosphine releases to atmosphere. Instrumentation is relied upon to shut down the process in the event of minor pressure excursions outside the normal operating envelope. Alternatives are emergency flares or alkali/hypochlorite scrubbers.

Emergency releases of phosphine are combusted, and the  $P_2O_5$  products directed to the plant stack.

#### (b) Electrolytic process

A diaphragm electrolytic cell can produce phosphine by the direct reduction of elemental phosphorus. This process is currently not commercially operational.

The cathode material must have a hydrogen over-voltage greater than that of platinum and metals such as mercury, mercury-cadmium amalgam or lead; graphite or stainless steel can be used for the anode. The electrolyte in both the cathodic and anodic sections is phosphoric acid.

The operating temperature is between 60 and 100°C. Phosphine is evolved at the cathode, and oxygen is produced at the anode.

Prevention of formation of 'spongy' deposits on the cathode and use of the diaphragm minimises hydrogen production. The electrolytic cell uses heavy metals including mercury,

cadmium and lead. Difficulties in controlling metal-emissions may be experienced.

#### (c) Potential release routes from the manufacture of phosphine

##### *Releases to air*

- Small amounts of white phosphorus, as phosphorus pentoxide, from raw material delivery.
- Phosphine from air blowing of liquid streams.
- Phosphine from pressure relief.

##### *Releases to water*

- 'Phossy' water from liquid white phosphorus storage.
- 'Phossy' water from condensing white phosphorus vapour.
- Water from phosphine gas holder seal.
- Scrubbing liquors.
- Filter aid from by-product phosphoric acid filtration.

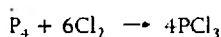
##### *Releases to land*

- Calcium phosphates and small amounts of phosphorus from treatment of liquid effluent streams.
- The destination of trace cationic impurities present in the phosphorus feedstock must be evaluated. Arsenic and antimony may be present in either the co-product phosphoric acid or the scrubbing liquors.
- Used filter cartridges.

### 2.7.5 Phosphorus trichloride

#### (a) Process description

Phosphorus trichloride ( $PCl_3$ ) is produced by the direct union of phosphorus and chlorine:



Liquid white phosphorus and gaseous chlorine are reacted in phosphorus trichloride liquid. A reflux condenser and fractionating column are located above the reactor.

Phosphorus is kept in excess in the reactor together with some phosphorus trichloride.

Phosphorus trichloride vaporised by the heat of reaction leaves the reactor via a distillation column and is condensed overhead. The majority of the distillate is returned to the column as reflux. The remaining distillate is sent to storage from the overhead receiver.

Gaseous emissions from the process consist principally of phosphorus trichloride vapour. The quantity passing to the

scrubber is 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. The gases are generally absorbed with water to give hydrochloric acid and phosphorous acid ( $\text{H}_3\text{PO}_3$ ) by hydrolysis.

Some installations use sodium hydroxide scrubbers; at others a water scrubber, due to the sharing of the scrubbing facilities with phosphorus oxychloride ( $\text{POCl}_3$ ) manufacture, is followed by a sodium hydroxide solution scrubber.

Phosphorus trichloride storage vessels are vented to a scrubber system, usually that of the reaction system. Drum filling operations are provided with air extraction around the filling lance, and this extraction is also scrubbed.

Overhead condenser practices vary with regard to coolant. Cooling water can be used, but there is a risk of water ingress and violent reaction. To minimise this risk, cooling water can flow over the tubes by gravity. Alternatively, heat transfer fluid or air-cooled condensers may be used.

Pressure relief of the reaction system is either by bursting disc to the scrubbing system or by bursting disc to an expansion or containment vessel. This in turn can vent directly or via another bursting disc to the scrubbing system.

Impurities present in the phosphorus feedstock accumulate in the reactor and are periodically removed. These residues include arsenic trichloride, antimony trichloride, and 'coked' organics from initial trace impurities in the phosphorus. By-product, phosphorus oxychloride (due to oxygen impurity in the chlorine) may also be present.

The impurities are periodically removed by cleaning out the reactor. After distilling out the phosphorus trichloride in the reactor to storage, cold water or dilute sodium hydroxide is added carefully to the reactor to decompose the remaining traces of phosphorus trichloride and other halides. The resulting liquor is discharged under controlled conditions to the effluent treatment plant.

#### (b) Potential release routes from the manufacture of phosphorus trichloride

##### Releases to air

- Small amounts of white phosphorus, as phosphorus pentoxide, from raw material deliveries.
- 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 air are small unless the scrubbing systems fail.

##### Releases to water

- Blanket 'phossey' water from liquid white phosphorus storage.
- Phosphorous acid and hydrochloric acid from wet scrubbing of phosphorus trichloride vapours.
- Metal halides; arsenic, antimony and 'coked' organics in wash liquors from cleaning reactors.
- All aqueous discharges are to a site treatment plant.

##### Releases to land

- Calcium phosphate and small amounts of phosphorus from site treatment plants.

#### 2.7.6 Phosphorus oxychloride

Phosphorus oxychloride can be manufactured by two routes:

- Reaction of a mixture of phosphorus pentoxide, phosphorus trichloride and chlorine
 
$$6\text{PCl}_3 + \text{P}_4\text{O}_{10} + 6\text{Cl}_2 \rightarrow 10\text{POCl}_3$$
- Oxidation of phosphorus trichloride with oxygen or air
 
$$2\text{PCl}_3 + \text{O}_2 \rightarrow 2\text{POCl}_3$$

##### (a) Chlorination process

A batch quantity of phosphorus pentoxide is added to phosphorus trichloride. Chlorine is then bubbled through the mixture.

Exothermic heat is removed by refluxing phosphorus trichloride via a distillation column and overhead condenser. Non-condensed vapours pass to a scrubbing system. As the reaction proceeds the phosphorus trichloride in the reflux is progressively replaced by phosphorus oxychloride.

Once the reaction is complete the chlorine supply is stopped. The batch is refluxed to drive off traces of free chlorine to the scrubber system, followed by distillation of the phosphorus oxychloride from the reactor to storage. Chlorine slippage can occur.

At intervals, 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. The residual dilute hydrochloric acid, containing metal chlorides and phosphoric acid, is directed to the site effluent plant.

##### (b) Oxygen process

Phosphorus trichloride is oxidised by oxygen or air in either a batch or a continuous process.

Batch operation is in an agitated reaction vessel with reflux condensers. Phosphorus trichloride is added to the reactor

and air or oxygen bubbled through the liquor. The heat of reaction is removed via the reflux condensers. Off-gases from the condenser pass through an after-condenser and are cooled by refrigerant to maximise the retention of phosphorus halides. The residual off-gases are directed to wet scrubbing.

Once the reaction is complete, the air or oxygen supply is stopped and the product filtered and sent to storage. Non-condensed vapours pass to the scrubbing system.

The equivalent process can be carried out continuously. 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°C and is passed to a second column for further reaction with oxygen.

This procedure avoids large temperature increases. Excess oxygen leaves via a cold trap for removal of phosphorus oxychloride and passes on to a wet scrubber system.

Wet scrubbing used to control gaseous emissions 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 is used for both plants.

### (C) Potential release routes from the manufacture of phosphorus oxychloride

#### Releases to air

- Phosphorus trichloride vapours from reactor charging, tank filling, breathing and pressure relief systems to wet scrubbers.
- Phosphorus oxychloride vapours from reactor, distillation, product storage and pressure relief systems to wet scrubbers.
- Chlorine from chlorine handling systems and slip in reaction and pressure relief systems to wet scrubbers.
- Hydrogen chloride from wet scrubbers.

#### Releases to water

- 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.
- All aqueous streams are directed to site treatment plants.

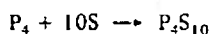
#### Releases to land

- Calcium phosphate from treatment of liquid effluent streams.

### 2.7.7 Phosphorus pentasulphide

#### (a) Process description

Phosphorus pentasulphide is produced by the direct union of white phosphorus and sulphur:



White phosphorus and sulphur are added as liquids in stoichiometric amounts to a pre-charge of phosphorus pentasulphide in a reaction vessel. Measure vessels are used to set the amounts of reactants. The elements react readily to form phosphorus pentasulphide and, after initial heat is supplied at start-up, the reactor is maintained at 380–400°C by cooling.

An inert gas atmosphere (carbon dioxide or nitrogen) is maintained in the reaction vessel and is discharged via a heat traced vent. Phosphorus pentasulphide vapours condense in the vent and reflux back to the reactor.

The exhaust gases in the vent are burnt to convert traces of hydrogen sulphide to sulphur dioxide before release to atmosphere.

Phosphorus pentasulphide liquid is fed to a flaker. Flaked product is transferred by a cooled screw conveyor for storage or packing. Some of the flaked product is ground into a powder and also packed. The flaker, grinder and conveyor are operated under an inert gas blanket, which discharges via a water seal. The packing operation has local air extraction. 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 distillation.

If vacuum distillation is practised, there can be a build-up of solid residues in the still. These will comprise of arsenic sulphides, and other metal sulphides which are disposed to landfill.

When phosphorus pentasulphide flakes are milled, some dust will be produced. This is recovered.

#### (b) Potential release routes from the manufacture of phosphorus pentasulphide

##### 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.

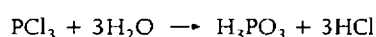


### Releases to land

- Phosphorus pentasulphide from spillages, cleaning of solids handling equipment.
- Residues from distillation unit.
- Calcium phosphate and small amounts of phosphorus from site treatment plants.

### 2.7.8 Phosphorous acid

Phosphorous acid is produced by the controlled hydrolysis of phosphorus trichloride:



The reaction can be violent, partly because of the heat liberated in the solvation of the hydrogen chloride. Process technology has been developed to overcome these problems by using:

- liquid-phase hydrolysis; or
- vapour-phase hydrolysis.

#### (a) Liquid phase hydrolysis

Phosphorus trichloride and dilute HCl are added continuously to an agitated reaction vessel. Hydrogen chloride evolved by the reaction is absorbed in water, collected in a strong acid absorber and recovered as a by-product acid.

The phosphorous acid/hydrochloric acid mixture overflows from the reaction vessel to the evaporator. Hydrogen chloride is evolved and recovered in a strong acid absorber. The concentrated phosphorous acid is solidified by a flaker and transferred by screw conveyor for packaging. The flaking and packaging operations are enclosed and performed with local extraction.

The hydrogen chloride is absorbed in a conventional cooled strong acid absorber in series with a weak acid tail gas absorber. The hydrogen chloride from the reactor system is cooled and passed through a demister before entering the absorption system.

Bursting disc pressure relief from the reaction vessel is via a drench scrubber to atmosphere.

#### (b) Vapour phase hydrolysis

Phosphorus trichloride liquid and water are atomised with steam in a coaxial atomiser and fed downwards into a reaction vessel at 150°C. Additional steam is supplied to the vessel to assist mixing. The vapours pass to a direct contact condenser/separator fed with phosphorous acid and the condensed product is fed to a vertical evaporator where most of the hydrogen chloride is removed to the absorption system.

Concentrated phosphorous acid leaves from the bottom of the evaporator and is stripped of residual hydrogen chloride by nitrogen stripping in a counter-current column. Pure phosphorous acid is sent to flaking.

Commercial-grade hydrochloric acid is a by-product of both processes. The hydrogen chloride in the tail gas absorber vent is essentially the only gaseous loss. In the direct contact process nitrogen stripping gas will leave the absorption system saturated with hydrogen chloride. The tail gas absorber design must cater for this flow, which will increase hydrogen chloride losses.

The management and recovery of dilute acid streams is more complicated for the liquid-phase hydrolysis process.

Phosphine is a possible thermal decomposition product of phosphorous acid in the direct contact process if the process is operated close to the thermal decomposition temperature.

#### (c) Potential release routes from the manufacture of phosphorous acid

##### 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 via drench scrubber systems.

##### Releases to water

- Liquors from wet scrubbing of vents from phosphorus trichloride storage.
- Surplus weak hydrochloric acid.
- Wash-downs and spillages, cleaning of solids handling equipment.
- All releases to site treatment plants.

##### Releases to land

- None.

### 2.7.9 Alkyl phosphonium salts

#### (a) Process description

Alkyl phosphonium ( $\text{RH}_3\text{P}^+$ ) salts are produced in a batch-wise exothermic process, aspects of which are considered commercially confidential.

The raw materials are metered in to a multiple agitated reactor system operated under slight positive pressure. On-line systems are in place to detect the end-point of the reaction.

The reactions produce by-product phosphine and phosphoric acid, which are vented via a combustion unit and scrubbing system.

The scrubbing system is monitored with alarms for flame failure, low flow and pump failure on the scrubber, and excess differential pressure on the mist eliminator.

Bursting disc failure would direct phosphine to the stack.

Prior to transfer to storage, the product is stripped to remove traces of reactants, which will form part of the aqueous discharge from the plant.

#### (b) Potential release routes from the manufacture of alkyl phosphonium salts

##### Releases to air

- Raw materials, by-products from storage, reactor, combustion unit and pressure relief.

##### Releases to water

- By-product acid from stripping.

##### Releases to land

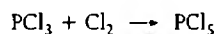
- Used filter cartridges.

### 2.7.10 Aryl phosphonic acids

#### (a) Process description

In the UK phosphorus pentachloride is produced batchwise in a carrier solvent for captive use in the production of aryl phosphonic acids ( $R'PO(OH)_2$ ).

Phosphorus pentachloride is produced by the reaction of excess chlorine with phosphorus trichloride:



The reactor is equipped with an agitator, cooling jacket and reflux condenser. Phosphorus trichloride is dissolved in about an equal volume of solvent in the reactor prior to commencing chlorination.

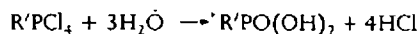
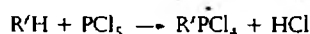
The solution is agitated and chlorine gas admitted. As the reaction proceeds, crystals of phosphorus pentachloride form and are suspended in the solvent. Reaction heat is removed by the reactor cooling jacket and reflux condenser; total reflux is employed.

Vapour emissions from the reflux condenser are passed to another condenser, cooled with refrigerant, to minimise solvent losses, and then to water and sodium hydroxide scrubbers to remove phosphorus trichloride and chlorine respectively.

Currently, solvents employed as a carrier are carbon tetrachloride (tetrachloromethane) and monochlorobenzene. The use of carbon tetrachloride should be supplanted by that of environmentally less harmful solvents.

The aromatic feed is reacted with the phosphorus pentachloride/solvent slurry and the chlorinated phosphorus

intermediate is hydrolysed to generate the substituted phosphonic acid:



The organic is added at a controlled rate via a measure tank. The exothermic reaction is controlled via cooling.

The solvent and hydrogen chloride are removed at elevated temperatures to condensers and scrubbers.

The solvent is collected by the condensers and stored for re-use. The hydrogen chloride is collected by the scrubber and stored for re-use, sold or forms part of the aqueous discharge.

The intermediate and any residual phosphorus pentachloride are hydrolysed with water at a controlled rate to generate a slurry. The slurry is filtered, the acidic filtrate forming part of the aqueous discharge and the semi-dry filter cake packaged for sale.

In the UK phosphorus pentachloride is not isolated for sale or use. The phosphorus pentachloride can be isolated by filtration with recovery of the solvent as filtrate. The crystals are dried by circulating hot water through the jacket on the filter. The solvent is recovered, and clarified and returned for re-use, and the product packaged for sale.

An alternative continuous process not using a solvent involves phosphorus trichloride being distributed from 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 extracted by mechanical screw.

#### (b) Potential release routes from the manufacture of aryl phosphonic acid

##### 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.

### **2.7.11 Alkyl/aryl phosphate esters**

#### **(a) Aryl esters**

For aryl phosphate esters  $((R'O)_3PO)$ , the aryl component may be a specific compound, eg an alkylated phenol, or a mixture, eg cresol and xylenol, depending on the product desired. These are reacted with phosphorus oxychloride:



When unloading phosphorus oxychloride from tankers, storage tank blanket nitrogen is vented to a water scrubber.

The reaction is batch operated; the phenol(s) and a catalyst are added to the reactor and heated to the required temperature before metered addition of phosphorus oxychloride. The reaction generates hydrogen chloride, which is directed to an absorber and tail gas scrubber.

The recovered 32–34% HCl is either re-used or sold.

Residual HCl in the product is stripped out at elevated temperature. The hydrogen chloride is absorbed in water and becomes part of the aqueous waste stream.

The crude product is transferred to storage tanks feeding distillation units.

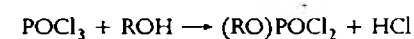
In the distillation units the excess phenolics are distilled off first and are recovered and transferred to storage for re-use. The product is then distilled and transferred to a steam stripping column. Residual waste organics, including the catalyst, are drawn off and drummed for dispatch as waste.

The product is steam-stripped 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 becomes part of the aqueous discharge from the plant.

The final product is transferred to storage.

#### **(b) Mixed esters**

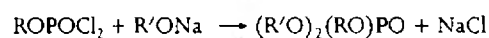
For mixed aryl/alkyl phosphate esters  $((R'O)_2(RO)PO)$ , the phosphorus oxychloride is reacted, first with an alcohol to substitute one chlorine molecule, and then with a phenol to substitute the other two chlorine molecules:



A set amount of phosphorus oxychloride is delivered to the reactor via a measure vessel. The alcohol is added at a controlled rate to the agitated reactor and the process is operated with a cooled recycle to control the temperature.

Once the reaction is complete the hydrogen chloride is stripped off to a scrubber where hydrochloric acid is produced, which is either re-used 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. The dichlorinated phosphate ester is added to the sodium phenate at a controlled rate, the temperature of the reaction controlled by cooling:



The crude product is washed to remove the salt, the washing forming part of the aqueous discharges.

The washed product is steam-stripped to remove trace organics, the steam is condensed and forms part of the aqueous discharge.

The product is filtered before dispatch to storage.

#### **(c) Potential release routes from the manufacture of alkyl/aryl phosphate esters**

##### *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 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.

**2.7.12 Control of releases from phosphorus processes****(a) Use and handling of phosphorus compounds****Phosphorus pentoxide ( $P_2O_5$ )**

Phosphorus pentoxide is neither combustible, nor supports combustion. It does however react 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. Care must be taken when disposing of empty drums that all  $P_2O_5$  is removed, since any remaining material will hydrolyse to phosphoric acid and severe corrosion may result.

Equipment for the transfer of  $P_2O_5$  from storage should be constructed of 316L stainless steel with PTFE gaskets or similar. The arrangements should be designed to eliminate any contact between  $P_2O_5$  and atmospheric moisture, either by equipping vents with dryers to dry any air or alternatively by continuously purging the system with dry air or dry inert gas.

**Phosphorus trichloride ( $PCl_3$ ) and phosphorus oxychloride ( $POCl_3$ )**

$PCl_3$  can be safely stored in carbon steel tanks with a minimum flow purge of dry nitrogen. The exclusion of moisture is important since  $PCl_3$  will react with water to form phosphorous acid and HCl.

Storage of  $POCl_3$  requires more sophisticated materials of construction than  $PCl_3$ . Steel and stainless steel are not suitable for long-term  $POCl_3$  contact. For storage of  $POCl_3$  only glass-lined steel or nickel tanks are recommended. Piping may be nickel, glass, glass-lined steel or Teflon-lined steel. Teflon lined plug or ball valves are normally used.

The unloading of either  $PCl_3$  or  $POCl_3$  causes fume to be expelled from the tank, and the use of a scrubber to control these fumes is considered mandatory. Water may be used as the scrubbing medium. The piping must be designed such that the scrubber cannot flood and back up into the storage vessel.

Overfilling the storage tank so that liquid  $PCl_3$  enters the scrubber will create a violent reaction producing HCl, phosphoric acid, phosphine and possibly fire. The packing could be ejected from the column. Elevated vent ducts and overflow seal legs can be used effectively.

**Phosphine**

Phosphine manufacture and handling is covered by CIMA Regulation<sup>(23)</sup>.

It is important to prevent oxygen ingress into phosphine production plant since this would present an explosion hazard. The process should be operated at slightly positive pressure with water seals between plant items and the environment.

Given the toxic and explosive properties of phosphine, storage should be designed to contain as small an inventory as practicable.

**(b) Gaseous effluent**

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 contaminants and their concentrations will depend on the manufacturing process. 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, for example phosphorus pentoxide from ignition of phosphine.

Fugitive emissions may be minimised by employing pressurised seals on agitated vessels and the use of glandless pumps when possible for product/intermediate transfers.

**(c) Aqueous effluent**

Effluents from phosphine plants should be blown with air to remove dissolved phosphine and then neutralised before passing to an effluent treatment system. Air from effluent blowing should be ducted into the plant ventilation system.

Aqueous phosphate emissions should be prevented from reaching controlled waters by precipitation with lime to produce insoluble calcium phosphate. The resulting sludge should be sent for landfill.

**2.8 Antimony, arsenic, beryllium, gallium, indium, lead, palladium, platinum, selenium, tellurium, thallium and their compounds****2.8.1 Introduction**

There is a very wide range of processes covered by this sector of the inorganic chemicals industry. Applications range from laboratory scale through to major chemical works 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 three groups of processes that describe several of the production routes encountered in this sector of the industry. Specific examples are given that involve some compounds of the elements covered by this Note. Some notes are added on other variations that may be found.

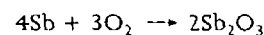
## 2.8.2 Manufacture of oxides

### (a) General

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 oil-firing may be practised.

### (b) Antimony oxide

Antimony oxide is manufactured by the roasting of antimony oxide concentrates with antimony metal. The reaction involved is:

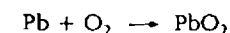
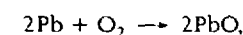


The process is carried out in direct-fired continuous rotary kilns operated so as to volatilise the product, which is then condensed and collected using fabric filters. After storage the antimony oxide is purified by revolatilisation in further rotary kilns followed by pure product collection, transfer, blending and packing. The slag formed during furnacing contains lead and is sold for smelting.

Special hygienic grades of product are made by damping, pasting or granulating antimony oxide with suitable plasticisers, water or waxes.

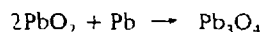
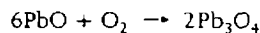
### (c) Lead oxides

The lead oxides, litharge (lead (II) oxide,  $\text{PbO}$ ) and red lead (dilead (II) lead(IV) oxide,  $\text{Pb}_3\text{O}_4$ ), 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:



The 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:



### (d) Lead acid battery grade oxide

The major use of lead worldwide (over 60%) is for the lead acid battery in the form of lead oxide. The principal process used for the production of lead oxide is that of Shimadzu, and this employs the continuous partial oxidation of lead pellets to give a closely controlled and intimate mixture of the element and lead monoxide/suboxide ( $\text{PbO}/\text{Pb}_2\text{O}$ ). 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 and response is likely to be necessary as fires have resulted from overheating of the product.

Battery manufacturers have their own specifications for the product oxide; a typical  $\text{PbO}$  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 smaller facilities use bought-in material. Some traction batteries and stand-by power batteries use red lead, which is made elsewhere as described above.

### (e) Selenium dioxide

Selenium dioxide is no longer manufactured in the UK.

### (f) Variations and associated processes

Other processes and techniques closely associated with furnacing include pre-treatment of feedstocks, product crushing, drying, blending and mixing, and dry materials handling such as mechanical or pneumatic conveying and packing.

Variations of the Shimadzu battery-grade lead oxide process outlined above are used; for instance the air-swept mill drum may be replaced by a perforated screen-mill drum. Here the principle is that product particles of the desired size fall through the perforations of the drum and are then classified by sieves before collection. Venting air is recirculated. 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.

In the battery industry, lead melting and casting for plates

and terminals, paste mixing, electrode plate pasting, flash drying, curing, stacking and insertion into battery cell containers will normally be associated processes and so form part of the Authorisation for the process.

#### (g) Potential release routes from the manufacture of oxide processes

##### *Releases to air*

- Where direct-fired processes are operated, products of fuel combustion are released, including oxides of sulphur, carbon and nitrogen.
- Particulate matter from furnacing and other unit operations and handling techniques involving metals and their compounds.
- The venting of lead processes, including melting/casting pots and battery electrode plate production and assembly operations, to meet workplace air standards, will release lead and its compounds.

##### *Releases to water*

- In the main, releases to water from these processes are cooling water discharges and plant wash-downs where practised; the latter will carry dissolved and suspended solids containing heavy metals.
- Processes carried out in aqueous solution may also release dissolved metal compounds in filtrates.
- In some processes, for example lead compounds manufacture, wet scrubbers are used to abate releases to air and this may result in the release of spent scrubber liquors containing the pollutants involved.

##### *Releases to land*

- Solid wastes recovered from fabric filters are recycled and slags should be reprocessed to recover useful heavy metals, eg by smelting, wherever possible.
- Other furnace wastes may require disposal where the useful content is too low.

### 2.8.3 General chemical and physical processes

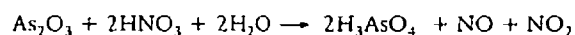
#### (a) General

General chemical and physical processes are used in the manufacture of many compounds of the elements covered by this section. These involve a variety of methods and unit operations, the majority of which are batch operations. The scale of the processes varies considerably with the nature and demand for the product concerned and major products are made on sizeable dedicated facilities, whereas minor products may be made by campaign working of multi-purpose plant.

#### (b) Arsenic acid

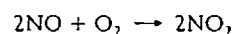
Arsenic acid ( $\text{H}_3\text{AsO}_4$ ) solution is manufactured by a process that demonstrates several unit operations typical of the industry:

- The feedstock arsenic trioxide is transferred from drums to the reactor feed hopper in a purpose-designed enclosed facility, which includes ventilation to a wet scrubber and drum washing. Material recovered from these is recycled to the process.
- Batch stirred reactors are used to react arsenic trioxide with 25–45% nitric acid. The reaction is isothermic and oxides of nitrogen are liberated:

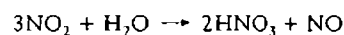


Potassium iodide catalyst may be used to promote the reaction.

- The mixed oxides of nitrogen are cooled, oxidised and absorbed in water. The reactions can be represented as:



and



The nitric oxide liberated during the absorption of nitrogen dioxide is oxidised again to nitrogen dioxide, using air as the source of the necessary oxygen. The nitric acid is recovered at concentrations from 25 to 45%, depending on the mode of operation of the absorption plant, and is re-used in the process.

- The product solution is cooled and press filtered to remove precipitated impurities (mainly calcium and lead compounds) before adjusting the concentration of arsenic acid to 80% by evaporation using steam coil heating. Finally it is transferred to storage and distribution tanks.

Alternative UK production facilities use different operating conditions, and employ sodium arsenite to remove residual nitric acid from the reaction mix. The arsenic acid is then filtered before use.

Arsenic acid is a basic ingredient for the manufacture of copper chrome arsenic (CCA) wood preservatives, which is essentially a mixing/blending process.

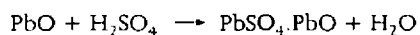
#### (c) Lead compounds

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 2.8.2(c)) 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 reaction vat and the required quantity of sulphuric acid is added:



- The resulting aqueous 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 stabiliser can then be transferred to mixers in which additives are mixed before packing to form a blended composite mixture for PVC processing.

Another 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. Sodium chromate is then reacted with the lead nitrate 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.

#### (d) Variations and associated processes

Other processes and techniques associated with the manufacturing routes used in the industry include those listed in Section 2.8.2.

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 followed by filtration, 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, which is followed by packaging.

Any gases that are evolved during reactions or precipitations are exhausted to caustic scrubbers.

Palladium and platinum compounds are made by appropriate variations to the examples above. For example, palladium chloride is manufactured by batch reaction of the element with chlorine in hydrochloric acid to form a solution that is evaporated to give a crystalline product. This is 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 separation and recovery, or catalyst manufacture.

#### (e) Potential release routes from the general chemical and physical processes

##### *Releases to air*

- Gaseous products of reaction, for example, oxides of nitrogen from the manufacture of arsenic acid, and hydrogen sulphide in the production of antimony sulphide.
- Excess gaseous reactants or evaporated media, eg chlorine and hydrochloric acid in the manufacture of palladium and platinum compounds.
- Particulate matter containing metal compounds, for example lead compounds in the exhaust air from flash drying and packing point hygiene units.

##### *Releases 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.
- Waste scrubber liquors generated in wet arrestment plant, alkaline or acidic depending on duty.

##### *Releases to land*

- Precipitated sludges and residues from aqueous effluent treatment processes containing metal compounds. These should be reprocessed to recover useful heavy metals wherever possible. For example lead precipitates can be recovered by smelting where metal values make it economic.
- Dust recovered from hygiene dust units where this cannot be recycled or reprocessed.
- Impurities removed from products by filtration, eg calcium and lead from the arsenic acid process.

#### 2.8.4 Compound semiconductor processes

##### (a) General

Several of the elements covered by this section are used in the manufacture of microelectronic semiconductor devices with 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. The major semiconductor technology area represented is the use of binary III-V materials (ie referring to the groups of the periodic table for the two elements used) as substrate wafers on to which successive thin-layer micro-circuits are deposited. These substrates provide some improvements over the use of silicon wafers in the specific applications for which their higher cost and safety/environmental demands can be justified.

Manufacturing processes based on silicon wafer technologies are not authorised under this sector.

The micro-circuits are created by the deposition of thin (of the order of 1  $\mu\text{m}$ ) 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 solvents including chlorinated hydrocarbons.

Inspectors should note that, although the scale of the processes used in the microelectronics industry is small, this is compensated for by the highly toxic and polluting nature of many of the materials used and the complexity of the plant installations. In particular gaseous hydrides, arsine and phosphine are used on most sites for circuit deposition. Highly efficient and reliable abatement techniques and operating procedures are essential. An Environmental Code of Practice has been published on behalf of the UK microelectronics industry<sup>(29)</sup>, and operators should be expected to adopt this as a part of their approach to environmental management.

#### (b) 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 formed 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 may be made by either the liquid encapsulated Czochralski (LEC) process or the gradient freeze technique. These are described below:

##### *LEC process*

The compound 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. This is slowly withdrawn 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  $\mu\text{m}$  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.

#### (c) Production of deposited circuits

Thin-layer micro-circuits are formed on wafer substrates by the deposition of successive layers of compound semiconductor materials composed of elements such as arsenic, phosphorus, gallium and indium. The principal process employed is known alternatively as metal organic chemical vapour deposition (MOCVD) and metal organic vapour-phase epitaxy (MOVPE). It 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. This results in the surface deposition or doping of micron or submicron thick layers of the materials in a defined epitaxial alignment. Deposition can be restricted to specific sites by photolithographic preparation of the wafer and/or subsequent removal from unwanted sites.

The process is carried out inside glove-boxes and is typically automatically controlled to allow the flow and hence deposition of an appropriate sequence of materials to provide the desired layering. Mainly these materials are obtained from gas cylinders, which are piped from remote storage cabinets to a manifold feeding the MOCVD/MOVPE reactor via flow restrictors and control valves. Hydride gases may be supplied in dilute (eg 15% arsine) form in hydrogen carrier gas or as 100% gas. Gallium and indium, when needed, are delivered in organic compound form, ie trimethyl or triethyl compounds. These are held as liquids through which carrier gas is passed to vaporise them. 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 require abatement before release. The process usually involves a main release point for excess reactants and a second release from the vacuum system that creates the low working pressure. Some commonly used abatement techniques are described below.

#### (d) Variations and associated processes

Certain micro-circuit deposition operations are carried out using other reactor techniques, usually involving ion implantation or molecular beam methods. These are used primarily where the substrate is a silicon wafer and the product is a special or tailored integrated circuit. These processes use and release significantly smaller quantities of arsine and phosphine reactants than the MOCVD/MOVPE process, but may generate in the reactor, especially if a plasma enhanced technique is involved, a number of significant gaseous breakdown products. Some of these may themselves be highly toxic and polluting. Therefore 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 carried out in clean-rooms and may involve



the use of perfluorocarbons (PFCs). These materials have a high global warming potential.

**(e) Potential release routes from the compound semiconductor processes**

*Releases to air*

- Particulate matter and gaseous compounds including metals and their compounds, for example excess reactant gases from the MOCVD/MOVPE process, including arsine, phosphine and silane. These may be oxidised during abatement.
- VOCs including chlorinated and fluorinated hydrocarbons.

*Releases to water*

- Liquids from wet abatement processes used for gaseous and particulate matter abatement, after appropriate treatment.
- Spent acids from etching processes used in micro-circuit production may be disposed of to sewer after pH adjustment.

*Releases to land*

- Spent filter units and carbon cartridges, also waste acid and solvent etchants may be disposed of to land.
- Materials recovered from treatment of releases to water.

**2.8.5 Control of releases**

**(a) General**

Many of the elements included in this sector exhibit significant toxic properties to man and the environment. The most widely used element is lead and its compounds, for which special considerations have been prepared. This is discussed below.

**(b) Lead**

The toxic properties of lead have long been recognised. Regulations covering all aspects of lead usage have progressively tightened. Strict controls now exist to govern the amount of lead discharged into the atmosphere. Modern factories have sophisticated extraction systems (often incorporating HEPA filters), which remove and filter dust and fumes. The dust is collected and fed back into the production cycle.

All aqueous wastes are usually collected and any lead removed and recycled where possible. Normal techniques used for waste-water treatment containing lead include chemical precipitation.

**(c) Gaseous effluent**

A great variety of abatement techniques are currently used within this sector of the inorganic chemicals industry as a result of the wide range of particulate, toxic gas, metals and VOC emission sources encountered.

There is wide usage of dry and wet particulate arrestment equipment such as cyclones, bag filters, HEPA's and wet scrubbing systems.

Owing to the extensive use of solids in many forms (ores, powders, granules, metals, stabilisers), local extraction ventilation (LEV) systems used to protect operators from workplace exposure and to maintain concentration levels of components below statutory guideline levels are much in evidence.

This results in a requirement to remove components from air extraction systems prior to discharge, and these can either be tied into process vents for abatement or treated separately depending on site layout, vent composition, etc.

**(d) Semiconductor industry**

High-technology abatement systems have been developed specifically for use in the semiconductor industry and special considerations are necessary.

Storage arrangements should be designed to give adequate security against leakage and have facilities for detecting and minimising any leaks that do occur. For example all toxic gas cylinders being used in semiconductor processes should be kept in sealed gas cabinets provided with exhaust ventilation and gas monitoring. Integral flow restrictions should be fitted to cylinders to limit maximum flow. Remote shut-off valves should be air-to-open with the air supply incorporating a plastic section that melts in the event of a fire.

Waste arsine or phosphine dopant gases from semiconductor processes can be abated by absorption with an oxidising agent such as sodium hypochlorite solution and acidified iodate or bromate solutions. Soluble salts form, which are retained in solution.

Activated carbon is used to control a variety of pollutants, including pollutants from the epitaxial deposition process used in semiconductor manufacture.

Incineration systems are also used.

**(e) Aqueous effluent**

Precipitation using lime, ferric hydroxide or ferric chloride is a common technique found in this sector to remove metals from aqueous waste streams.

Owing to the inherent value or harmful environmental effects of many of the species present in this sector, careful control, segregation and recycling of waste streams is practised.

**(f) Disposal to land**

Owing to the toxicity of many of the compounds/metals used in this sector, disposal to land is carefully regulated, with many wastes having to be identified as special wastes.

## 2.9 Cadmium and its compounds

### 2.9.1 Introduction

In applications where cadmium compounds are already encapsulated in a form incapable of causing harm (plastic granules, etc), they are not considered to be a use of cadmium compounds and hence do not fall within this sector.

### 2.9.2 Cadmium plating

#### (a) Plating process

There are a limited number of electroplating shops specialising in carrying out cadmium surface treatments. The number of these premises has reduced significantly in recent years to a baseline servicing a decreased product market. They range in size from operations using kilogram quantities to those using tonnage quantities of cadmium per year.

Regulations<sup>(2)</sup> restrict the use and sale of cadmium-plated materials mostly to safety-related applications in the aeronautical, aerospace, mining, offshore, nuclear and safety sectors. With this restriction, the number of premises carrying out cadmium plating has fallen.

Alternative surface treatments are available where some of the properties of cadmium plating are required, but no treatments are equivalent when all the properties of cadmium plating are required.

Cadmium plating is usually carried out at 15–30°C in alkaline cyanide solutions using cadmium anodes. The cadmium concentration in the cyanide solutions can be up to 25 wt%.

Cadmium plating of high tensile steels can be carried out in acidic cadmium fluoroborate to prevent stresses being formed in the steel.

Components being replated are stripped of their original cadmium coating, for example by using a solution of ammonium nitrate.

The plating process is usually preceded by a degreasing stage, which can involve shot blasting and caustic or chlorinated solvents either singly or in combination. Chlorinated solvents are often favoured as being easiest, quickest and of superior performance. However, the use of chlorinated solvents should be phased out in favour of other solvents and processes that are equally effective.

Components can be suspended in the bath for plating or, if appropriate, they can be 'barrel plated' by placing the components in a rotating basket in the plating bath.

After plating, components are rinsed in a 'drag-out' tank to remove the bulk of any adherent plating solution. In consequence, this part of the process usually has the greatest potential to give rise to a release of cadmium if recycle is not carried out. This is especially true in 'barrel plating' where the number/bulk of the components is liable to yield greater carry-over of plating solution.

Efficient drag-out and rinsing system designs minimise plating solution carry-over and water consumption, thereby minimising rinse water volume for treatment. Air blowing, spray and counter-current rinsing are examples of water conservation strategies, and rinse-water evaporation and re-use is an example of a recycle and concentration technique.

Owing to carry-over from the plating bath, solutions can become depleted in cadmium and require adjustment. This is achieved by the addition of cadmium compounds (either as solid or solution). Provided carry-over has been minimised, this adjustment is only occasional. Good handling techniques are used to prevent or minimise fugitive emissions.

Post-plating treatments include etching, passivation and brightening. Each ancillary process becomes contaminated with cadmium with the potential to bring about a release.

Cadmium plating lines should be segregated and banded. Wherever possible, all solutions and washes should be recycled. Several methods now exist to treat water containing cadmium to such a degree that the water can be recycled as process water. These generally consist of a bulk cation removal stage followed by polishing treatment. Cadmium in solution may be recovered by electroplating and concentrated by evaporation, membrane filtration, precipitation or ion exchange. This essentially gives a "zero emission to water" process, which is regarded as BAT.

#### (b) Potential release routes from cadmium plating processes

##### Releases to air

- There may be releases of cadmium compounds from the adjustment of plating baths, which is only carried out occasionally.
- Inspectors should consider possible releases as a result of any degreasing carried out prior to plating.
- Hydrogen cyanide could be emitted to air if cyanide-based-plating solutions are inadvertently acidified.

##### Releases to water

- Process waste streams may contain cadmium together with other metals and plating line additives or chemicals.
- Fully integrated treatment systems recycle deionised water for process use, recover cadmium metal for re-use and produce concentrated cadmium-containing liquors/sludges from ion exchange regeneration, membrane treatment or precipitation.
- Any such concentrate streams and stripping solutions can be treated further on-site or removed by licensed contractors. For some small operators it may not be BATNEEC to treat spent plating bath solutions and removal by authorised contractors should be justified.

**Releases to land**

- Where possible recovered cadmium should be recycled. Cadmium-containing sludges from effluent treatment should, wherever possible, be recycled for cadmium recovery; otherwise they may be disposed of as solid waste.

**2.9.3 Cadmium smelting**

The smelting process is covered by the IPC Guidance Notes for the production and processing of non ferrous metals.

**2.9.4 Production of nickel cadmium batteries**

There are currently no manufacturers of nickel cadmium batteries within the UK, although some assembly does take place.

**2.9.5 Pigment Manufacture****(a) Process description**

Regulations<sup>(25)</sup> restrict the use and sale of cadmium-based pigments in certain plastics mostly to safety-related applications.

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 maximises cadmium oxide recovery and gives a release to air meeting the new plant standard.

The oxide is converted to the respective sulphate by the addition of sulphuric acid. Alternatively, the sulphate can be generated directly by the action of sulphuric acid on cadmium metal.

Cadmium sulphide and optionally cadmium carbonate pigment is precipitated out by the addition of sodium sulphide and optionally sodium carbonate. The final colour can be adjusted by the co-current addition of zinc or selenium compounds during the precipitation stage.

The precipitate is obtained by filtration and the cake acid washed to remove any sodium sulphate.

The product is dried before being calcined at 540–610°C to convert the crystal structure to yield a pigment of the required colour. The product is again acid-washed and dried at this stage to remove any free cadmium or its oxide.

The pigments can be milled and blended to obtain the required grade of final product, which is then packed. Local extract ventilation exhausts via fabric filters.

**(b) Potential release routes from the manufacture of pigments****Releases to air**

- Cadmium oxide fume is released during the cadmium oxidation stage.
- Cadmium sulphide is released during the drying stage and final product packing.

- During the calcining operation, sulphur dioxide is given off.
- Particulates are abated using fabric and HEPA filters.
- Sulphur dioxide is removed by wet scrubbing with a basic medium.

**Releases to water**

- Spent liquors from the precipitation stage can, after treatment, be released to water. The effluent may contain cadmium.
- The effluent treatment systems used are a combination of those described in Section 3.4.

**Releases to land**

- Filter dusts, floor sweepings and effluent sludges contain appreciable quantities of cadmium and are generally suitable for recycle or recovery.
- Contaminated consumable material is generally suitable for landfill.

**2.9.6 Stabiliser manufacture****(a) Process description**

Barium/cadmium stabilisers are used particularly in PVC manufacture where they can form up to 3% of the mass of the polymer. Alternative compounds include barium/lead stabilisers.

Regulations<sup>(25)</sup> restrict the sale and use of PVC containing cadmium-based stabilisers mostly to safety-related applications.

Cadmium-based stabilisers, which are cadmium salts of fatty acids, are formed either from the reaction between the sodium salt of a long-chain fatty acid and cadmium chloride, or from the direct reaction of cadmium oxide with an acid in the presence of a high-boiling inert solvent. Only the second process is currently operated in Britain to produce a liquid stabiliser.

The reaction is carried out at elevated temperature and the water formed in the reaction is distilled off. The recipe for the reactor charge can vary depending upon the formulation required of the final product.

**(b) Potential release routes from the manufacture of stabilisers****Releases to air**

- Releases to air of cadmium oxide dust from raw material handling and volatile organic compounds from the use of high-boiling inert solvents. Cadmium oxide handling has local extract ventilation to atmosphere via fabric filters.

**Releases to water**

- Cadmium-containing distillate from the reaction may be

released after treatment with sodium hydroxide to precipitate cadmium oxide/hydroxide.

- Cadmium-bearing solids are reclaimed by filtration.

#### *Releases to land*

- Filter dusts, floor sweepings and filter cake containing cadmium compounds or organic solvents and which cannot be recycled.

### **2.9.7 Alloy manufacture**

Cadmium is used in many alloys to enhance mechanical, electromechanical and eutectic properties. These processes are covered by the IPC Guidance Notes in the Metals Industry Sector.

### **2.9.8 Ceramic Glazing**

#### **(a) Process**

Cadmium pigments can be used within the pottery industry to obtain bright red, orange and yellow glazes.

The glaze is applied as a suspension. Any excess is removed before the pottery passes to the furnace for firing.

Systems are now available whereby the area is segregated and all wash or cleaning waters are collected. Solids are separated out and the water recycled. This process then achieves a zero discharge to water and all the separated solids are returned for cadmium recovery.

#### **(b) Potential release routes from ceramic glazing processes**

##### *Releases to air*

- Heavy metals and volatile organic chemicals during firing.

##### *Releases to water*

- Cadmium from cleaning during glaze application, but see above.

##### *Releases to land*

- Damaged pottery and other contaminated waste containing cadmium pigment.

### **2.9.9 Control of cadmium releases**

#### **(a) Gaseous releases**

Cadmium-containing particulates and fume should be contained for recycle or recovery. Disposal should only be considered when the cadmium content is so low or the quantity so small as to make recovery impracticable.

Because of the limit on cadmium in releases to atmosphere and the particle size usually found in cadmium-laden fumes, cyclones and electrostatic precipitators are unlikely to be effective abatement equipment.

Fabric filters backed up by HEPA filters currently achieve the lowest emission levels of particulates from most cadmium processes and should generally be considered as BATNEEC. Applicants should be able to give sound technical reasons to support the use of other abatement techniques.

HEPA filters are able to remove submicron particles and emission levels of cadmium less than 0.05 mg/m<sup>3</sup> are readily achievable.

#### **(b) Aqueous effluents**

In all cases, aqueous streams containing cadmium should be segregated and BATNEEC applied with a view to recycling the stream or at least to minimising the release.

Technology now exists that allows some processes (eg cadmium cyanide plating and ceramic glazing) to segregate, treat and completely recycle aqueous streams containing cadmium. In these instances, aqueous releases are essentially zero or only occasional (eg partially treated ion exchange regeneration solutions). Any contaminants that build up or out-of-specification reclaimed cadmium that cannot be re-used must be periodically sent for disposal.

#### *Hydroxide precipitation*

Hydroxide precipitation is the most common process to remove cadmium from aqueous streams.

After settling, the resultant liquor is often filtered to remove any remaining solids and the sludge can be concentrated in, say, a decanter centrifuge or filter press to obtain a sludge with a solids content of 35%. This sludge, if other heavy metals are absent, is suitable for recovery of cadmium.

As cadmium hydroxide has a low solubility and due to the difficulty in filtering out all the fine precipitate, hydroxide precipitation cannot reach, on its own, the achievable levels for new plants and further treatment is required (eg sulphide precipitation and/or membrane filtration).

Hydroxide solubility varies markedly with pH and optimum conditions are essential for effective cadmium removal. Many plants where several heavy metals exist use pH 9–9.5 as being the optimum for overall heavy-metal precipitation. It is also within the normal maximum consent discharge to sewer limit of pH less than 10.

At pH-9 cadmium-hydroxide has a solubility of ~0.8 mg/l (as cadmium), which falls to 0.05 mg/l at pH 11.4. At higher pH other hydroxyl species are formed and solubility starts to rise.

Effluent treatment for cadmium hydroxide precipitation should therefore be operated at pH 11–11.5. However, 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.

In the plating industry where, for small operators, effluent streams containing a variety of components are routinely mixed, optimum conditions for cadmium removal may not exist but are selected with regard to the overall composition and discharge requirements.

### *Sulphide precipitation*

Sulphide precipitation is very similar in principle to hydroxide precipitation. It is more effective than hydroxide precipitation in that cadmium sulphide is very much less soluble than cadmium hydroxide. In the absence of other heavy metals and chelating agents the solubility of cadmium sulphide is less than 0.05 mg/l (as cadmium) at pH more than 9.

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/l) and cadmium sulphide is readily precipitated out. Control is required to ensure that there is not an excess of sodium sulphide to prevent any subsequent acidification releasing hydrogen sulphide fumes, which are both highly toxic and have a powerful characteristic malodour.

Iron sulphide is only very sparingly water-soluble (5 mg/l) and the problem of excess sulphide being present in the final effluent is generally avoided. However, due to the low solubility of the iron sulphide, reaction times are very long and the effluent treatment system needs very long residence time to ensure maximum cadmium sulphide precipitation. The design of the effluent treatment system needs to take this into account.

Owing to difficulty in removing by filtration all the fine cadmium sulphide particles, sulphide precipitation coupled with a simple filtration technique is unlikely on its own to achieve the guidance release levels for new plant.

### *Carbonate precipitation*

Carbonate precipitation relies on the low solubility of cadmium carbonate to remove cadmium from solution as a solid precipitate.

Precipitation is brought about by the addition of sodium carbonate to a pH of 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. This is thought to be due to sorption of cadmium onto the metal carbonate precipitate. The application of further treatment may represent BATNEEC.

The removal of the precipitate from the effluent is the same as that used for hydroxide and sulphide precipitation.

### *Electrochemical processes*

Several electrochemical systems of cadmium removal have been developed and are available commercially.

The modes of operation can vary, but essentially they utilise electrochemical techniques to transfer the metal ions in solution

to a cathode. In the plating industry this cathode can itself be used as the anode for electroplating, when a sufficient deposit has built up.

### *Ion exchange resins/macroehticlar resins*

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

Ion exchange can remove cadmium and cyanide from effluent. However, it does not destroy the cadmium or the cyanide, and a subsequent treatment of the regeneration solutions would be required.

### *Membrane processes*

Membrane processes used for cadmium removal include micro-filtration, ultra-filtration and reverse osmosis.

### *Cyanide destruction*

Many solutions for cadmium plating contain alkaline cyanide. This solution should be recycled wherever possible but waste streams can occur. Before techniques for cadmium removal are used, any cyanide present must be destroyed. This is to prevent the generation of toxic cyanide fumes at a later stage in the treatment process.

The most commonly used method for treatment of waste streams containing cyanide is oxidation under alkaline conditions. This can be achieved by a variety of techniques chlorination, ozonation, peroxide oxidation, or electrolytic oxidation and carried out in continuous, batch or closed loop systems depending on the specific characteristics of the waste stream to be treated.

New techniques include combining ion exchange with gas-permeable membrane technology for the removal of metals and cyanides from rinse waters.

The applicant needs to demonstrate existence of an adequate procedure to determine the completion of cyanide destruction (eg electro-potential).

## **2.10 Mercury and its compounds**

### **2.10.1 Introduction**

Outlined below (Sections 2.10.2 – 2.10.4) are three types of manufacturing process that use mercury or its compounds in a way that means they are prescribed processes. Specific examples are given of such processes; and notes are added, where appropriate, on other variations that may be found.

The wording used in Section 4.5(h) of the Regulations<sup>(1)</sup> means that any manufacturing process using mercury or its compounds may be prescribed; however, many processes only use very small amounts of elemental mercury at ambient conditions, with no planned releases to any environmental medium.

Such processes should be assessed for exemption from Part A control against the criteria given in the Regulations. Confirmation of a high degree of cleanliness and control, in compliance with HSE Guidance<sup>(10)</sup>, should be an important factor in considering exemption of a process.

Several processes in the chemical industry that use mercury or its compounds in a way that would render them prescribed processes may be most aptly described in other sections of the Regulations, for example as organic chemicals, halogen or pesticide processes. The respective Guidance Note for such processes should be consulted.

## 2.10.2 Manufacture of mercury compounds

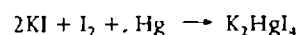
### (a) General

The manufacture of mercury compounds has declined very significantly in recent years as a result of both legislative and voluntary action following concern over the environmental effects of their use. Mercury-based pesticides and biocides, formerly made and used widely, have been progressively replaced by non-mercury alternatives. The final prohibition of all mercury-containing plant protection products was made effective by EC regulation in 1992<sup>(27)</sup>.

The majority of mercury compounds still used in the UK are imported. A limited number of mercury compounds are, however, manufactured for certain non-prohibited uses, eg in pharmaceutical products such as soaps, creams and for allowed fungicidal applications such as in paints used in tropical climates. These are typically manufactured from appropriate feedstocks in small stirred batch reactor systems.

### (b) Inorganic compounds

Potassium mercuric iodide is an example of an inorganic mercury compound. It is manufactured as a solution by a liquid-phase reaction from potassium iodide, iodine and mercury:



The process consists of dissolving batches of potassium iodide and iodine in water and then adding elemental mercury to the stirred reactor. The reaction is exothermic, but can readily be stopped from overheating by ceasing stirring and allowing the aqueous and mercury phases to separate. Following completion of the reaction and cooling of the product, it is packed directly from the reactor by transfer to drums.

The reactor is housed in a closed room and is totally banded, including the drum filling point. A common ventilation system is used to vent both the room and the reactor, the latter via a pot containing potassium iodide solution to reduce releases of mercury and iodine.

### (c) Organic compounds

Phenyl mercury compounds have been used for many years as bactericides or fungicides, eg in paints and wood preservatives. Although their use in products formulated and used in the UK

is believed to have ceased, manufacture for export continues at a significant level and may increase.

A process of manufacture of such compounds may, as noted above, be most aptly described as a pesticide process. But, if it does not meet the two specific criteria for such processes given in the Regulations<sup>(10)</sup>, it should be assessed for prescription as a process covered by this Note.

One such process that remains significant in the UK is that which produces phenyl mercuric dodecylsuccinate. This is made by a licensed process by a two-stage batch reaction from mercuric oxide, benzene, acetic acid and dodecylsuccinic anhydride in an organic solvent medium. The reactions are carried out in a stirred jacketed reactor, which can be steam-heated or water-cooled as required. The process includes a two-stage stripping of excess solvent, acetic acid and water, the first-stage strip being recycled to process but the second (mainly water contaminated with mercury) being sent for disposal with condensate and washing. The product is filtered to remove impurities and packed in drums within the plant area after adjusting to 10% mercury content in the solvent.

The liquid for disposal is treated by adding sodium hypophosphite to reduce most of the compounded mercury to the element. After a long settling period the supernatant liquor is transferred, neutralised and disposed of to suitable landfill. The elemental mercury is retained.

The reactor, packing point and first-stage effluent treatment are within a common banded area. The plant area is ventilated by a common fan, including the batch addition of mercuric oxide.

### (d) Potential release routes from the manufacture of mercury compounds

#### Releases to air

- Mercury vapour or particulate matter containing mercury compounds from reactor ventilation systems.
- Other feedstocks, particularly where dusty or volatile.
- VOCs from processes carried out in organic solvent media.

#### Releases to water

- Mercury-containing condensates, distillates and washing, after treatment, if it is not possible to recycle them to process and they are not disposed of to land.

#### Releases to land

- Contaminated packaging, wipes, process equipment and clothing.
- Insoluble impurities and mercury-containing liquids may be disposed of to land.

## 2.10.3 Mercury battery manufacture

The use of mercury in batteries, in the UK, will cease by the end of 1998.

## 2.10.4 Electrical equipment and instruments

### (a) General

Although declining in use generally, mercury retains a number of essential applications in a variety of equipment and instruments, including fluorescent discharge lamps, manometers and thermometers, control/switching systems, certain vacuum pumps, AC/DC rectifiers and gas-filled valves.

The processes used 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 contain the mercury.

### (b) Fluorescent discharge lamps

Mercury is used in all current mass production of discharge lamps worldwide and non-mercury alternatives are believed to be many years away from being developed to the stage of commercial viability. Mercury has a high vapour pressure at ambient temperatures and its use gives a high efficiency of luminosity/power consumed for white light applications. When excited electrically the mercury vapour atoms emit blue-green visible light and ultraviolet radiation. The latter subsequently excites the internal coatings of the lamp ('phosphors') to emit red-yellow light and hence provide a balanced output approaching that of natural daylight.

UK low-pressure discharge lamps typically each contain 10–20 mg of mercury, which is all vaporised when the lamp is made, but which gradually reacts with parts of the lamp until there is insufficient vapour to generate a complete discharge circuit. This may determine the life of the lamp and means that in their attempts to minimise mercury used per lamp, manufacturers are seeking to obtain a tight distribution of weights achieved. It may eventually be possible to reduce the weight to 6–8 mg in smaller products.

Mass production of low-pressure lamps is concentrated at a very small number of plants in the UK (possibly no more than four in total) and in Europe, with each manufacturer distributing products by an international network. Such plants mass-produce specific products, usually on a number of dedicated lines using the manufacturer's own detailed technology. The use of mercury in a typical process line 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 exhaustor machine. This is a multi-port carousel arrangement on which it is indexed to a number of staged operations; it is first evacuated, the air is then replaced by an inert gas and the cathode is energised to activate it.
- The lamp is heated to complete the drying of the coating, re-evacuated and replaced by inert gas at the required low working pressure.
- A metered droplet of liquid mercury is put in from a dispenser and the lamp is sealed by flaming. It is

subsequently energised, and lamps that fail to light or to remain lit are automatically ejected.

- Pure mercury (99.999%) is required for satisfactory lamp performance. This may be bought in as 'triple-distilled' mercury or it may be redistilled by the lamp manufacturer, as may any mercury recovered from exhaustor dispensers removed for maintenance, etc. Dispenser reservoirs are hand-loaded with fresh mercury as required.

### (c) Potential release routes from the manufacture of electrical equipment and instruments

#### *Releases to air*

- Mercury vapour is drawn into vacuum systems. These may expel directly to air or into general local exhaust ventilation.

#### *Releases to water*

- Providing an adequate degree of cleanliness and control is observed in the storage, handling and use of liquid mercury in compliance with HSE Guidance<sup>(16)</sup>, no release to water should occur.

#### *Releases to land*

- Rejected filled products where it is not practicable to recover the mercury, usually after breaking open by an appropriate method, eg lamp and tube crushers.
- Waste vacuum pump oil contaminated with mercury is disposed of to land as special waste. This arises from regular oil changes on the plant; also pumps may be returned to the suppliers for an annual overhaul and this will give rise to similar waste.

### (d) Variations and other processes

Other methods of loading mercury into lamps have been developed, which encapsulate the mercury until after the lamp has been sealed, thereby eliminating the release to air of mercury from the vacuum system. For example glass phials and amalgam strips are used successfully, and this might be considered to be BAT. However, a major investment in process and product verification is likely to be required for the conversion of an existing plant to such a system.

It is believed that specialist commercial and retail sign lighting suppliers may be making their own bespoke discharge lamp strips on their premises, using small quantities of mercury annually.

High-pressure fluorescent discharge lamps are made for commercial use on a much smaller scale than low-pressure lamps, using techniques that generally involve the injection of the mercury into a sealed lamp, and thus should not have a release of mercury to air.

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 of the latter include a type of domestic cooker thermostat still in production, mercury-in-glass, and mercury-in-steel thermometers. Most of these processes may well be exempted from Part A control; but careful attention should always be given to process vacuum systems and to local exhaust ventilation where used, as these are potential sources of mercury vapour releases to air.

### 2.10.5 Control of mercury releases

#### (a) Gaseous abatement techniques

Mercury levels in ventilation gases should be minimised by the use of sealed process systems wherever possible. Maintenance and operating procedures should be in place to minimise releases during all anticipated operations. Mercury in exhaust gases should be recovered and put to further use where this represents BATNEEC. This may include sale or re-use within the process.

It should be noted that mercury and its compounds have high vapour pressures generally and may be emitted from processes as vapour or a very fine aerosol (eg where a high temperature is involved). In these cases gaseous abatement techniques may be more appropriate instead of, or in addition to, particulate matter abatement.

Because of the limit on mercury in releases to air and the particle size usually found in mercury-laden fumes, cyclones are unlikely to represent effective abatement equipment.

#### Condensation

Condensation has the potential of being the simplest technique for recycling mercury and minimising waste. Where appropriate, condensation should receive strong consideration as the primary abatement technique, for example upstream of plant scrubbers and vacuum pumps. The recovered mercury should be capable of re-use or sale to the recovery sector.

Condensation is generally achieved by indirect heat exchange, eg in a shell and tube heat exchanger, with cooling water, possibly chilled. Coolant temperature should be justified with reference to the vapour quantity discharged, noting that elemental mercury solidifies at  $-39^{\circ}\text{C}$ . A typical temperature used in mercury recovery is  $-5^{\circ}\text{C}$ .

#### Adsorption

Activated carbon is used to control a variety of pollutants, including mercury. Specific adsorbents, such as sodium sulphide and sulphur-activated carbon, have been developed for the removal of mercury from a number of process exhaust streams

During the adsorption process mercury attracted to the carbon surface reacts to form mercuric sulphide, which is retained in the pores of the carbon granule. Up to 20 wt% of mercury can be collected.

Mercury adsorbent cartridges are available, which are designed to be used in filters for air and vacuum systems. In order to

adsorb mercury vapour successfully in systems that are oil-lubricated, oil mist must be removed by a separator upstream of the filter.

It is not normally practicable to regenerate mercuric sulphide-contaminated activated carbon in situ. The option of mercury recovery should be investigated.

#### Fabric filters

It is possible to improve the capture of mercury in fabric filters by the use of additives such as sodium sulphide, TMT-15 (a sodium salt complex) and suitable forms of sulphur-activated carbon such as pulverised coke from rotary hearth furnaces. These provide "target nuclei" onto which the mercury is adsorbed.

Mercury removal efficiencies of up to 90% have been reported for adsorption coupled with suitable filtration.

#### Wet collection devices

Wet collection devices may be used for mercury abatement, but a particular consequence of such methods is that a liquid effluent is generated that may require further treatment to achieve required effluent quality standards.

There is a known problem of the formation of potentially intractable finely divided amalgams being formed in scrubbing systems where other metals (eg silver) are present with mercury in exhaust gases.

It is possible, using an appropriate raw material or solvent as the absorbent, to recover mercury or partially reacted products such that they can be recycled to the process. For example, potassium iodide can be used to absorb mercury such that the resultant product may be used in a future production batch.

When such recycle to the process is not feasible, absorption may be carried out in such a way as to capture the mercury in an insoluble form to aid subsequent disposal. An example of this is the use of soluble mercuric chloride absorbent to precipitate mercurous chloride (calomel) from a gas stream containing mercury vapour.

#### Biofiltration/bioscrubbing

Micro-organisms including actinomycetates, bacteria, algae, fungi and yeasts have the ability to accumulate heavy metals, including mercury, from their external environment. Both—living and dead cells are capable of such accumulation, and specific organisms are able, for instance, to reduce cationic mercury to the element and catalyse  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ . Biological processes may offer a cost-effective process for the abatement of mercury, and, through the use of dead biomass or waste materials, enable the recovery of mercury for sale or re-use.

#### Aqueous effluent

In all cases, aqueous streams containing mercury should be segregated and BATNEEC applied with a view to recycle the stream or at least to minimise the release.



Because of the toxicity and persistence of mercury in the aquatic environment, a positive release system should be employed before discharge of treated effluent.

### *Oxide precipitation*

Oxide precipitation by the addition of calcium hydroxide, sodium hydroxide or magnesium hydroxide is a widely used process to remove high initial concentrations of mercury from aqueous streams. It relies on the low solubility of mercuric oxide in water.

After settling, the resultant liquor is often filtered to remove any remaining solids and the sludge can be concentrated in, say, a decanter centrifuge or filter press to obtain a sludge with a solids content of about 10%. This sludge, if other heavy metals are absent, is suitable for recovery of mercury.

As mercuric oxide has a solubility of over 50 mg/l at 25°C, and due to difficulty in filtering out all the fine precipitate, oxide precipitation cannot approach, on its own, the levels achievable by new plants, and further treatment is required. This may be carried out by the use of one or more oxide precipitation stages followed by precipitation of residual mercury as a sulphide using an appropriate reagent.

### *Sulphide precipitation*

Sulphide precipitation is very similar in principle to oxide precipitation. It is more effective than oxide precipitation in that mercury sulphides are very much less soluble than mercuric oxide. In the absence of other heavy metals and chelating agents, the solubility of mercuric sulphide is less than  $10^{-20}$  mg/l (as mercury). Sulphide precipitation is therefore used instead of oxide precipitation where the initial mercury concentration is below the minimum solubility for the oxide.

After pH adjustment, sulphide is added in the form of sodium sulphide, sodium hydrogen sulphide, iron sulphide or other milder forms such as sodium dithionites or dithiocarbonate.

Sodium sulphides are readily water-soluble (154 g/l) and mercury sulphides are readily precipitated out. Control is required to ensure that there is not an excess of sodium sulphide to prevent any subsequent acidification releasing hydrogen sulphide fumes, which are both highly toxic and have a powerful characteristic malodour.

Iron sulphide is only very sparingly water-soluble (5 mg/l) and the problem of excess sulphide being present in the final effluent is generally avoided. However, due to the low solubility of the iron sulphide, reaction times are very long and the effluent treatment system needs very long residence time to ensure maximum mercury sulphide precipitation. The design of the effluent treatment system needs to take this into account.

Different forms of sulphide also require treatment conditions for optimum efficiency in respect of pH; normally a specific figure in the range 5–8 is necessary, but each case requires evaluation.

Owing to difficulty in removing by conventional filtration all the fine mercury sulphide particles, sulphide precipitation is unlikely on its own to achieve the guidance release level for new plant. This may be achieved, however, by combining sulphide precipitation with one of either electrochemical techniques, membrane techniques or biological methods, described below.

The removal of the precipitate from the effluent is the same as that for hydroxide and sulphide precipitation.

Purpose-designed organic agents such as TMT15 (sodium salt complex) can also be used.

### *Co-precipitation*

Conventional precipitation techniques can be combined with flocculation/coagulation. The precipitating metal complexes adsorb onto the growing flocs and achieve residual metal concentrations below the solubility level of the precipitating system.

### *Chemical reduction*

Chemical reducing agents, including zinc, aluminium, iron, formaldehyde, formic acid, hydrazine and sodium borohydride or hypophosphite, may be used to recover elemental mercury from suitable aqueous wastes. Care is needed in the control and use of such agents and a follow-up technique such as described below (ie electrochemical, membrane or biological techniques) may be required to achieve the new plant standard.

### *Adsorption/ion exchange*

It is often difficult in practice to achieve the theoretical level of removal of heavy metals, including mercury, by a conventional chemical method unless this is followed by high-efficiency filtration which is assiduously controlled. Lower residual metal concentrations may be achieved by employing adsorption or ion exchange in addition to precipitation. The generation of suitable secondary precipitates onto which residual contaminants will adsorb by ion exchange may be used and such precipitates include ferric and aluminium hydroxides. There are also a number of absorbents that can be used to enhance filtration, eg montmorillonite (a hydrated silicate of magnesium) and zirconium phosphate or hydroxide.

Ion exchange processes may be used following suitable pre-treatment. Appropriate resins can remove ionic mercury from aqueous solution, with the advantage of giving less solids waste than other methods.

It is not expected that spent resins with adsorbed mercury will be regenerated and disposal to land followed by resin replacement is most likely. This is because ion exchange does not destroy mercury and regeneration eluent would itself require treatment.

### *Electrochemical techniques*

Mercury can be removed from solution by electrochemical cells. The problem of complexed or chelated waste water

can be overcome by using consumable iron electrodes, which break the complexes and co-precipitate ferric hydroxide with the mercury for subsequent removal.

### Membrane techniques

Advanced membrane techniques such as micro- and ultra-filtration and reverse osmosis are used in the treatment of heavy-metal wastes and may be applicable to mercury.

### (c) Disposal to land

Efforts should be made to reclaim mercury and other metals from wastes prior to disposal to land in order to minimise the quantities released. For instance, batteries, recovered sludges and dusts may be retorted to extract the mercury content; the recovery of mercury typically becomes feasible at 2% mercury content<sup>(7)</sup>. Lamps and tubes may be processed in purpose-designed crushing, cutting, sieving and distilling plants, which are used to separate glass, metal, luminising powder and mercury.

## 2.11 Compounds of chromium, magnesium, manganese, nickel and zinc

### 2.11.1 Introduction

The sections below outline groups of processes that describe a number of the production routes that may be encountered in this sector of the industry. Specific examples are given that involve some compounds of the elements covered by this Note.

### 2.11.2 Primary extraction from ore concentrates

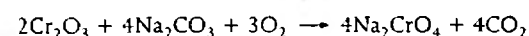
#### (a) General

The initial stages of some processes covered by this section involve the primary extraction of metal values from imported ore concentrates. A foremost example is the processing of chromite ore to primary chromium compounds. This is a large-scale continuous process using a combination of unit operations specific to the process route, and it is briefly described below.

#### (b) Primary chromium production

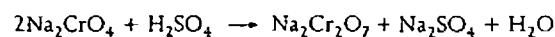
The primary chromium compounds, sodium chromate and dichromate, are manufactured using the 'zero lime' process for the conversion of the insoluble trivalent chromium contained within the ore to the soluble hexavalent form.

Chromite ore is roasted with sodium carbonate in a direct-fired rotary kiln under oxidising conditions at up to 1200°C. The ore is previously dried, ground and mixed with controlled proportions of sodium carbonate and recycled kiln residue which acts as a filler. In the kiln the trivalent chromium is oxidised to the hexavalent state:



The resulting crude sodium chromate is leached from the

hot frit in a quench tank and separated from the residue by vacuum filtration. Various impurities are chemically precipitated and removed to give a solution of pure sodium chromate ( $\text{Na}_2\text{CrO}_4$ ). Subsequently this is acidified to form sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ):



The product is obtained either as a solution or in a crystalline form. The by-product sodium sulphate is removed and purified in a reactor in which sulphur dioxide is used to reduce any residual hexavalent chromium. This is precipitated, separated and neutralised with sodium hydroxide to form chromium hydroxide, which is recycled to the kiln frit tank. The pure sodium sulphate solution is used to produce a crystalline by-product.

### (c) Associated processes

The process route involves significant associated processes and techniques. These include ore storage, pre-treatment of feedstocks, considerable materials handling and conveying operations; and the appropriate treatment of residues, recycles, by-products and wastes in all three media.

### (d) Potential release routes from extraction from ore concentrates

#### Releases to air

- Kiln exhaust gases contain products of combustion from gas or fuel oil. Particulate matter is entrained containing chromium (mainly unreacted chromite ore) and other feedstocks.
- Kiln frit quench tank vent gases contain hexavalent chromium and particulate matter.
- Exhaust gases from subsequent processes and kiln residue drying may also contain particulate matter including chromium compounds, as may local exhaust ventilation gases.
- Sulphur dioxide may be present in the sodium sulphate reactor vent gases.

#### Releases to water

- Normally no releases are made as the aim in operating the processes is to manage the water balance so as to contain and re-use all aqueous liquors containing soluble chromium compounds, for example all wet scrubber liquors and weak filtrates. These include liquors returned from the land filling of chromium kiln residue slurry.

#### Releases to land

- Wet chromium kiln residue containing unconverted trivalent chromium, alumina, ferric oxide and some occluded hexavalent chromium.
- Calcium carbonate and vanadate precipitates, also with

some occluded hexavalent chromium. These combined residues are treated chemically to render the waste non-hazardous before it is landfilled.

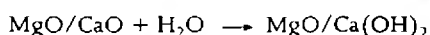
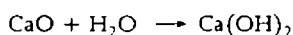
- Dusts that are recovered from all processes are recycled but spent filter bags may contain adhered chromium compounds.
- Waste packaging may be contaminated and old refractory linings, bricks, etc, will contain chromium compounds.

### 2.11.3 Extraction of magnesium from sea water

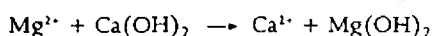
#### (a) Process description

A process route for the production of a number of magnesium compounds for refractory and other purposes uses sea water as a raw material from which magnesium hydroxide is precipitated. Magnesium oxide is subsequently produced by calcining the hydroxide. The process requires large volumes of sea water to win the magnesium because of the low concentration at which it is present. The process relies on simple chemistry and is outlined below.

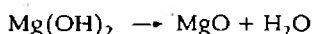
Calcium hydroxide, sodium hydroxide or dolime (calcium/magnesium oxide) are used as precipitants, depending on the final product required. The hydrations are carried out on-site using imported calcium oxide and dolime:



The required precipitant is added to settled and filtered sea water that has also been acidified with sulphuric acid and stripped of carbon dioxide in a tower. This precipitation is carried out in continuous stirred reactors:



The precipitate is settled out and washed in several stages with sea and fresh water before being filtered and dried as magnesium hydroxide product or fed to a kiln or furnace for calcining:



Alternatively, high-temperature calcining is used with a number of different additives to the feedstock for calcining to give specific products by reaction; for example, the addition of chrome yields a magnesium chrome spinel. A range of unit operations are involved, including wet-phase chemical reactions, washing, thickening, filtration, attrition, drying, calcining in rotary and multiple-hearth furnaces, and packing.

#### (b) Potential release routes from the extraction of magnesium from sea water

##### Releases to air

- Kiln and furnace exhaust gases contain products of combustion from gas or fuel oil, coal and coke.

Particulate matter is entrained, principally magnesia but also containing chrome, silica and oxides of iron and calcium.

- Similar particulate matter is also released from fuel, raw material and products handling operations and local exhaust ventilation systems, including dust from the hydration of calcium hydroxide and dolime.

##### Releases to water

- The main used sea water discharge contains suspended solids, principally magnesia, but also solids as listed for release to air.
- Sea water used for washing of magnesia contains similar solids as do plant and area washing, which may carry other solid releases including calcium hydroxide and dolime and product materials.
- Returned sea water used for the wet scrubbing of rotary kiln exhaust gases contains dissolved/reacted products of fuel combustion as well as suspended solids as above.

##### Releases to land

- Waste packaging, spent filter bags and refractories, which may contain magnesia.

### 2.11.4 Production of pigments and oxides by calcining

#### (a) General processes

Compounds of the elements covered by this Guidance Note are used in the preparation of many industrial pigments. The processes involve the calcining of a wide variety of feedstocks, for example metal oxides, sulphates, chlorides, fluorides, nitrates and carbonates. This is usually carried out in direct-fired tunnel, static or intermittent kilns or rotary furnaces, which are mainly gas-fired. Indirectly heated (eg induction) furnaces may be used and these may give lower releases.

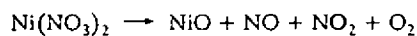
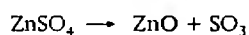
However, tunnel kilns are traditionally used in the pigment industry and here the feedstocks, which are controlled blends of raw materials, are batch heated for long periods in saggars (small refractory crucibles). Rotary kilns are also used, for example in the manufacture of chromium oxide for pigment and metallurgical uses by the continuous roasting of a mixture of sodium dichromate and ammonium sulphate.

A typical production route is outlined below:

The dry raw materials are handled from sacks or drums and are weighed and mixed in predetermined proportions to obtain the required shade of pigment after calcining. Local exhaust ventilation is used extensively during these operations.

The blended powders are added to saggars, which may contain 10–20 kg each, and these are heated in the furnace for the required time and at a specified temperature, for example 24 hours at 1000°C. During this period, especially early in the

cycle, gases are released as the metal compounds decompose to the oxides by reactions such as:



These are given as typical examples only; the actual reactions will vary depending on the mix of raw materials and the conditions used.

The product consists of a number of metal oxide complexes. It is allowed to cool and then processed into the final form by operations such as dry or wet crushing, washing, filtration, granulation and drying. The product is packed for sale or, if it is a base colour, may be blended or mixed with glass frit for use as a glass enamel.

#### (b) Potential release routes from the production of pigments and oxides by calcining

##### *Releases to air*

- Products of gas combustion and calcining. In batch kilning processes the release of the latter will generally vary as calcining proceeds; substances released may include hydrogen, ammonium chlorides and fluorides and oxides of sulphur, carbon and nitrogen. The gas stream may contain particulate matter including metal compounds and other gaseous or particulate pollutants, depending on the feedstocks and reactions.
- The production of chromium oxide may additionally release some hexavalent chromium and ammonia.
- Particulate matter containing metal compounds may be released from local exhaust ventilation systems serving feedstock, product handling and processing operations, primarily those performed dry.

##### *Releases to water*

- Waste liquors from product washing containing many dissolved and suspended metal compounds, also similar liquors from plant and process wash-downs. High concentrations of ionic salt species may be present, especially sulphate and fluoride.
- In the chromium oxide process, wet scrubber liquors are recycled to frit quenching. Filtrates from the product filters are treated on a washing plant from which a proportion is recycled with the remainder passing to final effluent treatment before release.

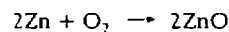
##### *Releases to land*

- Reject pigments, dust from bag filters and metal compound precipitates (mainly hydroxides) from effluent treatment.
- Used saggars and refractory brick linings.

## 2.11.5 Production of metal oxides by direct oxidation

### (a) General

Some metal oxides are produced using routes that involve the direct oxidation of the element, usually to give a finely divided powder product. Of the processes covered by this Note, the principal example is the production of zinc oxide. This is carried out by two alternative process routes, direct and indirect, as outlined below, both using the simple reaction:



### (b) Direct process

The direct process starts with impure zinc oxide such as oxidic ore concentrates and/or oxidic residues. This is converted to zinc vapour in a reducing atmosphere and then re-oxidised under controlled conditions in a combustion chamber. Feedstocks include zinc oxide oversize, galvanisers ashes and diecasters ashes and these are mixed with industrial-grade coke. Rotary kilns are generally used in a batch or semi-batch mode for the reducing process.

### (c) Indirect process

The indirect process, used to give various specific grades of zinc oxide including high-purity product, predominates in the UK. In this process, pure metallic zinc in ingot form or zinc from secondary sources is melted, vaporised, burnt and the zinc oxide collected. The type of feedstock and processing technique used depends very much on the specific grade of product being made. A variety of furnaces and associated plant are used in these processes; the furnaces include indirect-fired crucible box types, direct-fired muffle types, rotary kilns and electric resistance heated furnaces. The latter have the advantage of lower releases but operating costs may be higher. Zinc is melted at 600–650°C and burnt at about 1000°C.

The zinc oxide product from both processes is air-cooled and collected on bag filters, which also act as arrestment plant.

### (d) Potential release routes from the production of metal oxides by direct oxidation

##### *Releases to air*

- Products of combustion of gas, coke or oil, including oxides of sulphur, carbon and nitrogen.
- Particulate matter, mainly zinc oxide, in the exhaust from product conveying and collection.
- Local exhaust ventilation from handling of product or raw materials, which may contain some impurities from the zinc feedstock such as lead or cadmium. These are minimised by using high-grade feedstock and maintaining the molten zinc temperature as low as possible.

##### *Releases to water*

- There should be none from these processes.

### Releases to land

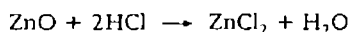
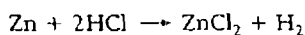
- Depending upon the feedstock nature and purity, solid residues are produced containing zinc, iron, aluminium, copper or lead as well as inert silicates. Wherever possible these should be re-used in the process or sold for recovery of metal values.
- Other waste may include old refractory linings, crucibles and retorts, spent filter bags with adherent metals and waste packaging.

### 2.11.6 General chemical and physical processes

General chemical and physical processes are used in the manufacture of many metal compounds; and involve a variety of methods and unit operations, including chemical reaction, precipitation, evaporation, separation, drying, mixing, grinding, classifying and packing. Specific products employ process routes made up of a number of these operations and associated techniques using continuous or batch operations. Processes vary considerably in scale depending on the nature of and demand for the product concerned. Major products are made on sizeable continuous dedicated facilities, whereas minor products may be made by campaign working of multi-purpose batch plant. Some examples are outlined below.

#### (a) Zinc chloride

Zinc chloride, which has a number of important industrial uses, is produced both in anhydrous powder form and as a solution. It is made from zinc metal and oxide residues from the galvanising industry. The process starts with physical separation of the feedstocks by milling and classifying to produce zinc metal slabs for sale, leaving zinc oxide and some metal to be reacted with hydrochloric acid to form the chloride in solution:

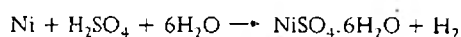


Hydrogen liberated by the first reaction is released to air. A natural draft chimney above the reactor keeps its concentration in the gas space below the lower explosion limit.

The solution is filtered to remove acid-insoluble impurities. Soluble metallic impurities are then oxidised and displaced before being removed in a further filtration stage. The zinc chloride is either sold, or concentrated by evaporation to higher-strength solutions, or concentrated to anhydrous product by vacuum evaporation to dryness.

#### (b) Nickel sulphate

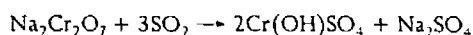
Nickel sulphate is an important chemical with uses in the metal plating industry and in catalyst manufacture. It is made worldwide by a number of routes, including as a by-product from the electro-refining of copper. In the UK the process used relies on the reaction of pure refined nickel with sulphuric acid to produce the hexahydrate:



Nickel pellets are added to sulphuric acid in a recirculatory reactor until the required strength is obtained. The solution is then filtered to remove impurities, crystallised and the product is centrifuged, washed, dried and packed. The hydrogen generated in the reaction is used in the primary nickel process.

#### (c) Chrometans

Chrometans are chromium chemicals used widely in the tanning industry where animal hides are treated with them to produce leather. They vary in exact composition but usually contain basic chromium sulphate produced by the reduction of sodium dichromate. This may be carried out in different ways and in the past was often done at tanneries using sulphuric acid and a suitable easily oxidised organic compound such as glucose. However, it is believed that direct reduction using sulphur dioxide has superseded this entirely for UK chrometan production:



The sodium sulphate by-product is not separated but forms part of the tanning agent.

For large-scale production, sulphur dioxide is made in situ by sulphur burning, while smaller processes may use imported liquid, which is gasified. The reaction is conducted in absorption towers with counter-current contact of gas and liquid, usually with external cooling to prevent boiling, since the reaction is strongly exothermic. Chrometan solution is produced and this is sold after dilution or is dried to give a powder product. Organic compounds such as oxalates and formates may be added to simulate the organically reduced product if required.

#### (d) Potential release routes from the general chemical and physical processes

##### Releases to air

- Specific gaseous products of reaction or excess reactants, for example oxides of sulphur or nitrogen, hydrogen sulphide, hydrogen chloride and ammonia.
- Particulate matter containing metal compounds, especially from dry handling and processing stages.
- Soluble and insoluble metal compounds from wet arrestment devices.
- In the example given of zinc chloride manufacture, hydrogen is formed when residual zinc metal reacts; and this carries some hydrogen chloride with it. Hydrochloric acid fumes may arise from storage of the acid.
- The handling of feedstock zinc oxide and anhydrous zinc chloride may release particulate matter containing these materials in conveying air and local exhaust ventilation.

- In the production of chrometan some unreacted sulphur dioxide is released to air, although two-stage counter-current absorption is used to minimise this.
- Off-gases from the drying of nickel sulphate contain some particulate matter carried over, and this is arrested by a cyclone followed by a wet scrubber.

#### *Releases to water*

- Process effluent liquors containing metals and their compounds in solution and suspension, mineral acids and other substances used in specific processes.
- Waste scrubber liquors generated in wet arrestment plant; these may be neutral, alkaline or acidic depending on duty.
- In the case of zinc chloride, some of the product may be contained in waste vacuum pump seal water and condensates from evaporation, while zinc oxide and hydrochloric acid may be present in scrubber liquors.

#### *Releases to land*

- Precipitated sludges and residues from aqueous effluent treatment processes containing metal compounds, mainly as hydroxides. Wherever possible these should be re-used in the process or sold for recovery of metal values.
- Other waste may include spent filter bags with adherent materials, waste packaging and reject products unsuitable for reprocessing.
- The zinc chloride process outlined above gives rise to filter cake residues, which contain metallic zinc, lead, aluminium, iron, copper and manganese. Also zinc hydroxide arises from effluent treatment. These residues are washed or dewatered as appropriate and disposed of to land.

### **2.11.7 Control of releases**

Conventional treatment techniques are widely used within this sector of the inorganic chemical industry. For example, cyclones and bag filters are widely used for the abatement of dust emissions, and chemical precipitation techniques are used for aqueous streams to remove metals. The following operations require special consideration.

#### **(a) Furnacing**

Where a furnacing process is involved, the choice of type of furnace to be used should take into account the releases that may occur. For instance electric induction and resistance furnaces will not release direct products of fuel combustion to air. Such furnaces are successfully used in the manufacture of zinc oxide. They may offer higher thermal efficiency and closer temperature control than fuel-fired furnaces and should be considered by applicants for new plants.

Combustion products, as a result of the use of furnaces/kilns, require special consideration within the sector.

#### **(b) Chromium**

Where hexavalent chromium is present, it should be reduced to the trivalent state before precipitation and disposal. This can be achieved by adjusting the pH to the required acid value and adding a reducing agent such as sodium metabisulphite. Such a waste stream should normally be kept separate from other wastes until this step has been carried out, although in some cases it may be desirable to use the acidity in another suitable waste stream to reduce the pH.

## 3 Best available techniques for controlling releases

### 3.1 Introduction

This section covers techniques for controlling releases that are common to many processes or are considered to be general in their application, ie are aspects of overall management of a works to minimise releases to the environment.

The standard techniques for pollution abatement are outlined in various reference sources including:

- Air Pollution Advisory and Review Group<sup>(28)</sup>, reports;
- BAT Review Reports on Pollution Control;
- HMIP/EA Technical Guidance Notes relating to IPC; and
- Environmental Technology Best Practice Programme (ETBPP), guides<sup>(29)</sup>.

These techniques need to cover releases from raw materials reception/storage, internal transportation, processing, and waste materials storage pending disposal.

The processes should be designed and operated in such a way that the substances released have the minimum impact on the environment. As a general principle, there should be evidence that the releases of prescribed substances will be prevented, or minimised and rendered harmless, and that releases of other potentially harmful substances will be rendered harmless: this should then be confirmed by conditions in the Authorisation. Since the priority is to prevent releases, emphasis should be placed on the avoidance of processes and abatement techniques that create wastes.

An applicant should have reviewed all available options (prevention, minimisation and recycling procedures<sup>(30)</sup>) and have demonstrated that the selected combination of production process and abatement equipment represents BATNEEC, and that the concept of BPEO has been satisfied.

More details of the methods available for preventing or reducing releases are listed in Research Report No P182<sup>(31)</sup> on pollution control in the inorganic chemicals industry. The most important techniques for the inorganic chemicals industry include, but are not restricted to, those given in Section 3.2 and 3.3.

### 3.2 Management techniques

Effective management is central to environmental performance and is an important component of BAT. It requires an actual commitment to establishing objectives, setting targets, measurement and revision according to results. This systematic approach may be aided by the achievement of management standards such as ISO 14001 and EMAS<sup>(32)</sup>. The following sections provide information on the main types of management technique.

#### 3.2.1 Senior management commitment

The commitments made by companies that sign up to the Responsible Care<sup>(33)</sup> or similar initiatives provide a good framework for the implementation of management techniques. The key aspects of this Initiative, which companies should be committed to through their senior management, and which they should be able to demonstrate they are applying, are that:

- all health, safety and environmental impacts of activities, products and processes have been identified and considered;
- there is a commitment to conform with statutory regulations as a minimum and to work with authorities to develop and implement measures where needed;
- employees and contractors are aware of the commitment and are involved in its delivery; and
- they are open with information both inside and outside the organisation.

A company might not be a formal signatory to the Initiative but could still be expected to be aspiring to its principles.

#### 3.2.2 Organisation and responsibility

There should be a clear structure for managing environmental issues in general and ensuring compliance with the Authorisation in particular. This should be fully integrated with the process operator's wider company and site decision-making systems. Many sites have a management committee and it would be expected that the environment is represented on it and discussed at regular intervals.

There should be a clear contact point for the IPC Authorisation: usually this requirement can best be met by having a single point contact. This should be seen as clarifying the interface between Agency and process operator. It should not reduce the responsibilities of other members of staff for ensuring compliance with the Authorisation.

The environmental performance of the process is highly dependant on the attention and awareness of the process operator's staff. They should be aware of this and their role in this performance made clear. The company should reinforce the message that environmental protection matters to the company. One way to do this is to have environmental performance as a part of annual performance assessments.

Incidents have occurred in the past resulting from poor communication among operations staff during shift changes and maintenance or other engineering work. Specific procedures should be in place to avoid such problems.

The planning and scheduling of batches can influence waste production and the company operating the process should be

able to show that these opportunities have been considered and, where favourable, implemented.

The overall environmental performance of the process should be monitored, and the results should be considered on a regular basis and form part of the management assessment process. Environmental performance indicators (EPIs) could be used for this purpose, although the potential difficulties of deriving them for rapidly changing batch operations should be recognised.

A contingency plan should be in place which identifies the potential types of incident that could occur and provides clear guidance on how they will be managed and who is responsible. In some circumstances these will need to be notified to the Agency as a condition of the process Authorisation and these must be clearly defined. Procedures should be in place to identify, respond to and learn from all complaints and incidents.

### 3.2.3 Maintenance

A programme of preventive maintenance should be in place.

Records of process performance should be available and used to monitor slow changes in releases that may signal the need for maintenance.

All staff should be aware of the role they can play by maintaining vigilance, for example, in relation to process upsets and leaks, and appropriate procedures should be in place to encourage staff involvement.

A procedure should be in place to authorise modifications and to undertake checks after modifications before process start-up.

### 3.2.4 Process control

The operator should be able to demonstrate that the process is being adequately controlled. In many cases this will involve the use of a computer-based system with facilities to ensure control in emergency situations.

As noted above there should be records of production and a procedure in place to ensure that they are subject to periodic review.

### 3.2.5 Waste minimisation

Waste minimisation audits should be conducted periodically to a defined programme. The Institution of Chemical Engineers, amongst others, has issued guidance on waste minimisation<sup>(30)</sup>, whilst a number of Waste Minimisation Clubs have been set up, eg Aire and Calder.

The active participation of staff should be encouraged in these initiatives, with recognition given to those who identify waste minimisation improvements.

There should be active monitoring of materials throughput, and mass balances should be available for processes. Monitoring should include water, power, heat and solvent use.

### 3.2.6 Design

The environmental implications of a new process or product should be considered at the earliest stages of the project and should continue to be reviewed at regular intervals thereafter. This is the most cost-effective time to introduce improvements in overall environmental performance. There should be evidence that alternative process options were considered and assessed. It should be possible to maintain an audit trail of the design and decision-making process.

### 3.2.7 Training

All staff should be aware of the regulatory and statutory implications of the Authorisation for the process and their work activities.

Training should be given to all staff involved in process operation and this should include the environmental implications of their work and the procedures for dealing with incidents.

There should be records of the training given to all staff.

### 3.2.8 Finance and accounting

There should be a good understanding of the costs associated with waste production within the process. This can be achieved by having accounting practices in place that ensure that waste disposal and other significant environmental costs are attributed to the processes involved and are not treated simply as a site overhead.

The process operator should be able to demonstrate that adequate resources are being committed to keep the process operating in compliance with the Authorisation.

## 3.3 Minimisation and abatement of releases to air

### 3.3.1 General

Releases to air from the processes authorised under this sector have a wide range of properties that can influence the choice of abatement technique. These properties include but are not limited to:-

- high temperature;
- particulate laden;
- odorous;
- combustion products ( $\text{NO}_x$ ,  $\text{SO}_x$ );
- acidic gases;
- toxic gases;
- VOCs;
- "wet"; and
- metal vapour/metal dusts.

A wide range of techniques are therefore applicable and can be found in operation in this sector. Often a combination of techniques (for example cyclone/fabric filter/HEPA or venturi scrubber/packed tower) is required to abate emissions successfully.



The aim should be to maximise material recovery, minimise flaring and minimise releases by applying appropriate techniques. The release of prescribed substances to air during plant cleaning, equipment decoking, catalyst regeneration, catalyst discharging and disposal, and catalyst charging operations should be prevented. Metals and their compounds in exhaust gases should be recovered and put to further use where this represents BATNEEC. This may include sale or re-use within the process.

VOCs, unless required for further processing, should be put to constructive use where possible. This may include sale, or use as fuel for gas turbines, heaters, furnaces, boilers, etc.

Means for reducing sulphur oxides, oxides of nitrogen and particulate matter should be considered using the techniques described in IPC Guidance Notes S2 1.01<sup>(17)</sup> for large combustion plant and S2 5.01<sup>(34)</sup> for the chemical incineration processes.

Any credible abnormal events, including activation of emergency pressure relief devices, that could lead to release of materials to atmosphere, should be identified on the application, giving the likely frequency of the event, quantities released, chemical species involved, their concentrations and discharge rates.

Means for dealing with polluting releases from pressure relief systems should be provided. Such means normally include phase separation where two-phase flow is possible and may include venting to scrubber systems, to flare, to vent, or to an enclosed dump tank. Procedures should be in place to reduce to a minimum the likely frequency of such releases. It may be appropriate to have two relief devices in parallel set at different relief pressures. The relief device at the lower set pressure may be of a smaller capacity, which can relieve small excursions such that the maximum capacity of the relief device is capable of being scrubbed in emergency equipment. The relief device at the higher set pressure would be sized for the low-probability-high flowrate event that cannot be abated and must be released at a sufficient height to promote dispersion, prevent hazardous concentrations at ground level, in buildings or plant structures, and protect the process system integrity.

For emergency vent releases that could have a significant environmental impact, total containment relief systems should be considered. This would require a vent receiver that does not discharge directly to atmosphere and is capable of receiving the complete process gaseous, liquid and solid inventory, taking account of all decomposition products, without itself being overpressurised.

Fugitive losses of volatile compounds can be substantial and can go unidentified unless a programme of leak detection and repair is in use. For most of the more hazardous materials, engineering standards exist to ensure minimal leakage and are specific to the substance. Best available techniques for the prevention of such losses in general include the following:

- use of high-integrity valve, pump and compressor seals;
- use of canned or magnetically driven pumps;

- minimising the use of flanged connections;
- use of caps or plugs on open-ended lines; and
- provision of closed loop flush on sampling lines.

Raw materials, intermediates and products with a true vapour pressure (TVP) of 14 kPa or above at maximum run-down temperature or odorous substances should be stored so as to minimise releases to air. Techniques available include fixed roof tanks with internal floating covers and rim seals, fixed roof tanks (with or without gas blankets) venting to suitable arrestment plant, or pressure storage. Suitable arrestment techniques are condensation, absorption, adsorption and destruction. If thermal destruction is chosen, then the installation of flame arresters or other deflagration/detonation safeguards may be necessary. In general bulk storage temperatures should be as low as practicable and temperature changes due to, for example, solar heating should be taken into account.

Some compounds have low odour thresholds. Therefore the control of odours should be an integral part of the pollution abatement systems.

For batch operations it is generally difficult to balance the flow of gaseous wastes to minimise peaks and troughs of releases the operation of a common gas collection system facilitates a more constant supply to gas treatment equipment and may be enhanced by appropriate scheduling of the operation of different processes.

Heating or cooling circuits should be monitored where appropriate for process fluid contamination. Temperature alarms should be fitted to prevent overheating/cooling.

Lagging should be fitted where this would minimise energy usage, material degradation, or fluctuations in temperature.

Secondary releases can result from the collection and open treatment of waste water containing volatile compounds as a result of direct and indirect contact. Direct contact occurs when:

- water is used to wash impurities from products in reactors, pipelines, etc.;
- water is used to cool or quench vapour streams;
- condensed steam from steam ejectors pulling vacuum on vessels containing such compounds;
- water is used as a carrier for catalysts and neutralising agents (eg sodium hydroxide solution); and
- water is formed as a by-product from reactions.

Consideration should be given to pre-stripping of the waste water or use of an enclosed treatment method. Vented vapours should be passed to appropriate treatment plant.

Where plants are enclosed for toxicity purposes, generally

large extraction volumes are used to prevent build-up of toxic vapours to ensure plant and personnel safety. Such large air volumes with low emission concentrations do not lend themselves to abatement. Total plant enclosure with low extraction volumes going to abatement plant, with large extraction volumes being available in the event of more substantial emission, should be considered. The applicant should justify the regime it is intended to employ and, where abatement is not being used, it should be demonstrated that suitable dispersion will be obtained in all situations and that the installation of abatement equipment would entail excessive cost.

Releases of VOCs may occur from cleaning processes or reactions using solvents. The operator should be able to demonstrate that the solvent selected is the least environmentally harmful, and all practicable precautions to minimise VOC releases and to render any such releases harmless have been taken within the context of BATNEEC.

The dilution of process vents by mixing with general extract air is not generally considered to represent BATNEEC. An applicant wishing to use this procedure should demonstrate that it represents the BPEO as opposed to applying abatement to the concentrated process stream.

Notwithstanding the provision of relief catch tanks, applicants should demonstrate that all practicable steps have been taken to prevent the occurrence of a runaway reaction. On the basis that, in most cases, one reactant is added at a controlled rate to the full charge of the second reactant, important considerations include the following:

- Operating procedures should ensure that the reaction is properly initiated and under control before the main reactant addition stage, which is often on automatic control, commences.
- If initiation of the reaction is known to be a problem, impurities in the feed materials should be minimised.
- The flow of the input reactant should be limited such that the heat of reaction evolved cannot exceed the capacity of the reactor cooling system.

### 3.3.2 Particulate matter

Solids handling operations can be encountered where charging, discharging, conveying, storing and packing of solid raw materials and products are undertaken. In all cases, equipment design should ensure that there is the minimum of dust generation and reliance is not solely placed upon dust extraction and treatment plant.

Specific techniques that have proven successful in minimising the generation of dust-laden gas streams when handling dusty solids include the following:

- Manual weighing out from raw material containers under local extraction.
- When having to charge solids by hand to a vessel charge

hole or manway, using a local extraction venting outside the vessel rather than ventilate through the vessel to minimise dust entrainment.

- Charging complete drums of solids by means of flexible fabric seals between drum and vessel, so that there is no net displacement volume or need for extraction.
- Dissolving sacks charged directly to the vessel.
- Enclosed automatic sack or drum handling plant.
- Drum filling devices that fill from the bottom upwards to eliminate the free fall of solids through the air in the drum.
- Attaching the polythene flexible liner of the drum around the neck of the filling device to contain any dust.
- Charge chutes and/or hoppers to reduce solids impact velocity.
- Water jet solids pump for use with recirculatory charging systems.

Where a dust-laden gaseous stream is generated by a process, the stream may require abatement equipment fitted to reduce dust losses. The application should show why dust has been entrained by a gaseous stream and that this effect has been minimised at source.

The methods available for minimising or reducing discharges of particulate matter to the atmosphere include:

- cyclones;
- fabric filters;
- high-efficiency particulate arresters;
- ceramic filters;
- wet collection devices;
- electrostatic precipitators, both wet and dry; and
- dust suppression equipment.

Further information is available in Technical Guidance Note A3<sup>(9)</sup>.

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. The solids or slurries recovered should be re-used where practicable.

#### (a) Cyclones

Cyclones are the principal type of gas solids separator, employing centrifugal force, and are widely used. They can be manufactured from a wide range of materials; and can be designed for high-temperature and high-pressure operation. Cyclones are suitable for separating particles down to about 5 µm; smaller particles down to about 0.5 µm can be separated where agglomeration occurs. High-efficiency cyclones are capable of removal efficiencies of the order of 90% for particles down to 5 µm.

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  $\mu\text{m}$ . 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 first-stage treatment method for solids removal in a particulate abatement system.

Cyclones can be irrigated to reduce levels of dust re-entrainment.

A new concept in particulate filtration, the inertial filter, claims to achieve high removal efficiency by the use of an impeller that is rotated at speed within an enclosure. Dust-laden air from the process enters the enclosure and the larger particles are immediately ejected 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 are immediately rejected. This dynamic barrier inhibits the passing through of particulates. The efficiency of the unit in any one instance can be modified by changing the speed of the impeller.

### (b) Fabric filters

The industrial fabric filter is generally constructed from a woven material or a felted fabric to provide the filtration medium through which the particle-laden gases are passed. Fabric filters may be constructed from multiple layers of different materials to produce the required filtration efficiency.

Filter efficiency/ease of cleaning may be enhanced by pre-coating the filter cloth. Coatings such as PTFE may be used. Conventional filter elements rely upon a steady build-up of particulates that contribute to the efficiency of the filter, ie filtration efficiency increases over time as particulates build up to a peak, after which it falls off due to progressive fouling. With PTFE-coated filtration elements, the filtration efficiency is high at the start, and can be maintained in this way by ensuring that particulates do not build up on the filter element. These do not rely on the contribution of the particulates to the filtration efficiency. The release characteristics of PTFE also reduce fouling and increase cleaning efficiency.

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

Regular maintenance and cleaning of the filters is necessary to maintain removal efficiencies. However, the operation of units has improved with the implementation of variable blowing sequences for filter bag cleaning using electronic pulse timers. This system can be remote-mounted in a control panel rather than in situ. The sequence may also be controlled by a PLC. 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. Excessive cleaning not only uses excessive compressed air, but can result in shortened bag life. Broken-bag detectors are available that reduce the impact of fugitive emissions. Also units are available complete with emission monitoring systems to monitor ongoing performance and quantify releases should they occur.

The performance of fabric filters may be assessed by measuring the dust concentrations upstream of the filters and in the exhausted gas stream. Bag failure should be alarmed, or at the very least regularly checked for using differential pressure transmitters or manometers.

A wide range of types of fabric filters are now available and 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.

It is unlikely, however, that fabric filters on their own will achieve BATNEEC standards for heavy-metal fume with particle sizes of less than 1  $\mu\text{m}$  diameter. If used for these applications, fabric filters may need to be backed up by other devices, eg HEPA filters.

An example of this is in the production of red lead where a fabric filter/HEPA filter arrangement is used following a cyclone.

Fabric filters are also available in cartridge form. Compared to filter bag, cartridges have a larger filtration area, and are generally smaller units. In some cases the same equivalent filter area can be achieved with half the number of elements.

Conventional bag and cartridge filters are rated for use up to 180°C. Cartridge filtration is often more efficient than bag filtration. Some fabrics have been developed that are able to withstand temperatures up to 250°C.

### (c) High-efficiency particulate arresters

HEPA filters exist in several forms and self-cleaning versions are now available. Generally the filters consist of a bed of densely packed fibres (often spun-bonded polymers) or sintered material to provide the filtration medium through which the particle-laden gases are passed.

Owing to the density of packing and the type of fibres, HEPA filters are capable of achieving high removal efficiencies for particles of 0.5  $\mu\text{m}$  diameter and larger. They can also remove a significant proportion of particles down to 0.01  $\mu\text{m}$  diameter.

HEPA filters are not generally suitable for use in moisture-laden streams due to the adverse effects of 'blinding'.

The condition of HEPA filters can be monitored by pressure drop measurement to show when the filter is becoming blocked. Pressure drop monitoring can also demonstrate the occurrence of filter failure or incorrect sealing of a filter.

HEPA filters have the disadvantage of high pressure drop (relative to wet scrubbing) and can therefore be unsuitable for large airflows where the required size of filter leads to a

comparatively high capital cost when compared to other systems.

Self-cleaning versions use a reverse air pulse system similar in principal to fabric and ceramic filters.

#### (d) Ceramic filters

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

The high-density units generate a higher pressure drop than the lower-density type.

Ceramic filters may also be constructed from other materials, which include metal and metal "fibres", sintered metal or granulated activated carbon cloths. Where more robust filters are required that can withstand corrosive gases, an all-metal filter with a sintered nickel membrane incorporated into a stainless steel housing is available.

Ceramic filter elements are now capable of withstanding temperatures in excess of 1000°C, instantaneous temperature shock from 900°C to 0°C and thermal cycling.

Filtration efficiencies greater than 99.9% for particulates down to submicron sizes are attainable.

Regeneration is achieved by reverse air pulse at about 7 barg, 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.

#### (e) Wet collection devices

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

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

In a venturi scrubber the gases are drawn into the throat of a venturi tube to which pressurised water is injected. There are two basic types: low and high pressure drop. Pressure drops at the lower end of the range (250 mm water gauge) are generally adequate for the removal of particles of a few microns in diameter.

For submicron particles the upper range of the pressure drops (1500 mm water gauge) may be required, particularly if collection efficiencies greater than 99% are required.

The separation efficiency of venturi scrubbers is dependent on the high relative velocity between the particulate-laden gas stream and the scrubbing liquor in the venturi throat.

Efficiencies can be increased by saturating or supersaturating the gas stream prior to the scrubbing section.

Satisfactory operation of scrubbers should be properly controlled and confirmed by measurement and, where appropriate, recording of the necessary parameters. These may include: exhaust gas analysis, gas or scrubber liquor pressure drop and temperature, liquor circulation flowrate or level and liquor composition, eg pH, redox potential or solids content. The choice of scrubbing medium depends upon the nature of the pollutant to be abated; a neutral medium may be used where only insoluble particulates are involved, whereas acidic or alkaline media should be employed for neutralisation as is appropriate.

Although not as efficient in particle removal as HEPA filters, wet scrubbers have the advantage of a lower pressure drop and therefore may be appropriate in situations where large flows are encountered. The applicant should be able to demonstrate that the large airflow is necessary (eg for safety reasons). The preferred option would be to contain the system to require a smaller volumetric airflow, so allowing the use of a fabric/ceramic filter with a HEPA filter second stage.

#### (f) Electrostatic precipitators

Electrostatic precipitators (ESPs) of the wet or dry type can provide very high collection efficiencies of dust or fume particles down to 0.01 µm diameter and can operate at high temperature (up to 450°C) or high humidity, unlike bag filters. ESPs may be preceded by a conditioning tower to optimise performance and may be designed with low pressure drop and thereby reduced power consumption of induced draught fans. Compact units are available for small applications and cleaned air may be recirculated to the process instead of exhausting preheated or pre-cooled air to atmosphere.

The disadvantage of electrostatic precipitators is the risk of sparking off explosions of flammable gas mixtures. This limits the application of electrostatic precipitators, particularly for processes using organic solvents.

A new type of filter has been developed known as a turbulent precipitator. Air containing particulates passes over the filter medium and generates a static charge, which attracts and holds dust particles. This unit can be used for very hot gases, and for the removal of fine solid or liquid particles from gas streams. It has many similarities to an electrostatic precipitator, but does not use electricity.

**(g) 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.

**3.3.3 Gaseous effluent abatement techniques**

The methods available for minimising or reducing discharges of gaseous substances to the atmosphere likely to be appropriate for the processes covered by these Notes include the following:

- condensation;
- absorption
  - packed and plate tower scrubbers,
  - spray towers,
  - wet mop scrubbers and rotacloves;
- thermal decomposition
  - thermal incineration,
  - catalytic incineration,
  - flares;
- adsorption
  - activated carbon adsorption.

This is not an exhaustive list of acceptable techniques and, as other systems are developed, they should be evaluated for individual processes.

**(a) Condensation**

Condensation has the potential of being the simplest minimum-waste-producing abatement technology, capable of recycling substances. Where appropriate, condensation should receive strong consideration as the primary abatement technique, for example upstream of plant scrubbers.

Condensation is generally achieved by indirect heat exchange, eg in a shell-and-tube heat exchanger, with cooling water, possibly chilled. Coolant temperature should be justified with reference to the vapour quantity discharged.

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

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

Condensation will generally only be applicable to batch/continuous processing operations where particulates

are not present and where concentrations of condensible components are significant.

Cryogenic systems can also be used in certain applications.

**(b) Absorption****General**

Where a soluble gas is released from a process, abatement techniques should be used to prevent or reduce emissions of the gas to the atmosphere. Usually this is achieved by scrubbing in a wet scrubber, a technique that has proven effective in removing a wide range of species either by solution in water or by absorption in aqueous acid or alkaline solutions.

The absorbent may be recycled round the absorber or passed to a recovery system.

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

- maximum interfacial contact between gas and liquid phases is maintained;
- sufficient residence or contact time for absorption is allowed; and
- the contaminant is readily soluble in the absorbent.

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

It should be noted that wet collection devices can be used for these purposes as well as for particulate matter control.

Consideration should be given to using an absorbent that can be used directly in the same process, for example by using an appropriate raw material or solvent as the absorbent to recover solvent or partially reacted products. They can then be recycled to the process, or used elsewhere, eg using water to absorb hydrogen chloride or oxides of nitrogen such that the resultant hydrochloric or nitric acid is of sufficient strength to be used as a process raw material or for effluent treatment. It is likely that a secondary scrubber designed primarily for minimising releases to atmosphere will be required in those cases, using a reacting absorbent liquor.

For multi-product batch plants the scrubber should be designed to abate the worst-case release with the lowest scrubbing liquor concentration. Often it is appropriate to have an on-line second scrubber although the scrubbing liquor in the second scrubber will require careful monitoring.

Instrumentation and alarms should be installed to ensure that liquid level and flowrate are maintained and that the pressure drop remains constant. Low-temperature alarms may be

necessary to warn of freezing. Where appropriate, concentration of absorbent should also be monitored. Scrubbers should include sample points upstream and downstream to allow analysis of inflow and outflow gas concentrations.

In absorption equipment, 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 the BPEO where the absorption process concentrates the potential release into the absorbent and makes recovery for re-use, sale, or treatment easier.

### *Packed and plate tower scrubbers*

In a packed tower scrubber the packing material provides a large surface area for mass transfer between liquid and gas phases. In the plate column the plate disperses the gas into numerous bubbles, so creating a large surface area for mass transfer. The even distribution of scrubbing liquor and prevention of plugging or channel flow is of critical importance to the satisfactory operation of such a system.

The advantages of packed tower scrubbers include generally modest to low pressure drops, and ease of construction with chemically resistant material. A wide variety of different packing geometries and materials of construction are now available.

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

Variations include high-efficiency gas scrubbing packed tower systems based on a fluidised-bed design. High turbulence in the gas flow is caused by fluidising the packing, and the counter-current gas and liquid streams are therefore brought into intimate contact, significantly enhancing the mass transfer characteristics of the system. Significant reductions in the height and diameter of the system can be achieved and the system can also remove particulates without encountering the conventional solids blockage problems of a packed tower system.

### *Spray towers*

Spray towers can achieve good removal rates for readily absorbable contaminants. Mass transfer is achieved by atomising the absorbent using nozzles and may be enhanced by the use of appropriate surfactants.

The simple design allows relatively easy construction in corrosion-resistant material and ease of maintenance.

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

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

### *Wet mop scrubbers and rotacloves*

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

Rotacloves operate in a similar manner to wet mop scrubbers except that the impeller is rigid. Rotacloves tend to be used for higher flowrates, wet mop scrubbers for lower ones. The polarity of the surface of the adsorbent determines the type of vapours for which the adsorbent has the greatest affinity.

## **(c) Thermal Decomposition**

### *General*

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

Three basic decomposition processes can be employed: thermal incinerators, catalytic incinerators, and flares. Process boilers can also be used in certain circumstances. The applicant should justify the choice of process.

In the inorganic chemicals sector, use of these processes is limited, but thermal incineration is practised in specific applications; for example it is used in some processes to remove hydrogen sulphide. The applicant should justify the choice of processes.

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

Considerable fuel savings can be realised by use of heat recovery systems. The following technologies should be considered:

- **Recuperative** – direct heat transfer between the exit gas and the incoming feed stream; up to 70% of the energy in the product gas may be recovered.
- **Regenerative** – use of a direct-contact ceramic heat exchanger alternately contacted with hot product gas and the cool incoming feed stream; the cyclic process affords very high energy recovery, up to 95%.
- **Waste energy recovery** – additional heat exchangers can be added to provide process heat in the form of low-pressure steam and/or hot water.

### Thermal incineration

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

For example, waste gases containing arsine gas and other arsenic compounds in the hydrogen carrier gas stream leaving the production reactor of the MOCVD/MOVPE process used in semiconductor manufacture can be controlled by thermal incineration.

The temperature of the incinerator, oxygen concentration and the gas residence time are the most important operational variables. Most thermal units are designed to provide no more than one second of residence time to the waste gas with typical temperatures of 650–1100°C. Once the unit is designed and built, the residence time is not easily changed, so that the required reaction temperature becomes a function of the particular gaseous species and the desired level of control. A support fuel is normally burnt to maintain the desired temperature. Reference should be made to the Waste Incineration IPC Guidance Note S2.5.01<sup>(9)</sup> for further details, including achievable release levels.

### Catalytic incineration

Catalytic incinerators employ a bed of active catalyst material to facilitate combustion of the pollutants. The catalyst has the effect of increasing the reaction rate, enabling conversion at lower reaction temperatures, typically 150–500°C.

Catalysts are now available that are poison-tolerant and suitable for removal of hydrogen cyanide, hydrogen sulphide and chlorine-containing VOCs.

For optimal operation, the volumetric gas flowrate and the concentration of combustibles in the gas flowing to the catalytic incinerator should be constant.

New catalysts based on heavy metals are being developed for use in catalytic devices.

Proprietary thermal/catalytic cartridge cracking columns are successfully used to abate hydride gases from the ion-implantation-type semiconductor processes.

### Flares

Direct combustion or flaring can be used for the destruction of intermittent or emergency emissions of combustible gases. Whilst there may be 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.

The flare system should be carefully designed to an internationally recognised standard to allow combustion of all gases necessarily vented to it under all gas flows, and wind dilution should be considered and allowed for in the design. Flares should burn without smoke under all conditions and should be designed to accommodate varying flowrates.

The applicant should justify flare heights.

Knock-out pots/drums should be installed as close as practicable to the flare to catch liquids and condensible material.

Problems associated with flare systems include the following:

- The heat generated may be unacceptable without careful design.
- The light/luminescence of the flame may be a nuisance if the plant is near an urban settlement.
- Flare tip mixing systems can cause increased noise levels.
- Incomplete combustion can result in the emission of toxic or obnoxious substances.
- Flares need to be kept lit constantly with robust pilot lights. Procedures should be operated to ensure that the pilot lights do not fail.
- Heat cannot be recovered.
- Constant purging is generally required.
- Monitoring of releases from flares is generally impracticable, making it difficult to ensure adequate combustion.

Flare gas recovery systems should be considered to minimise flaring.

### (d) Adsorption

#### General

Adsorption describes the removal of gaseous components from a gas stream by adherence to the surface of a solid. The gas molecules removed are referred to as the adsorbate and the solid to which the molecules adhere is the adsorbent. Adsorbents are highly porous materials.

Adsorption is used for air purification and solvent recovery. The most common adsorbents are activated carbon, silica gel, activated alumina and zeolites.

The polarity of the surface of the adsorbent determines the type of vapours for which the adsorbent gas has the greatest affinity.

Polar adsorbents will preferentially adsorb any water vapour present in the gas stream. If moisture is present in gaseous waste streams, their application to pollutant removal is limited.

Of the above-mentioned adsorbents, activated carbon is the only common non-polar adsorbent. Therefore, further discussion is based on activated carbon systems.

#### Activated carbon adsorption

Carbon beds may be of fixed-bed or rotary wheel design, regenerative or non-regenerative. In all cases the contaminated

gas stream should be pre-treated to remove any particulate matter or entrained liquids. High humidity can also interfere with the adsorption process. Humidity levels may be reduced by a combination of cooling of the gas to condense out water vapour followed by heating of 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. Pipework should be designed to allow simple and efficient changeover between beds. A variation of this multiple-bed system sees two carbon beds in series. Changeover between the two beds is initiated when breakthrough of the first bed occurs. Regeneration is achieved by low-pressure steam or warm air.

An alternative to fixed beds is the rotary wheel using a carbon matrix. Contaminated air is passed through 90% of the wheel, which is rotating slowly, so adsorbing the pollutants, with the clean air discharging to atmosphere. By means of a series of specially designed seals, hot regenerating gas is passed counter-currently through the other 10% segment and the pollutant is driven off. Such systems are normally employed to concentrate a pollutant stream before passing to an incinerator. 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.

As a general rule adsorbers operate below 55°C. Any increase in pressure will increase the adsorption capacity of a system. As the temperature increases, the capacity of an adsorbent decreases, since the energy level of the adsorbed molecules increases. This gives them sufficient energy to overcome the van der Waals attraction and migrate back to the gas phase.

The residence time in the adsorber is dependent on the gas velocity (the slower the gas passes through an adsorber, the greater the probability of a contaminant molecule hitting an available site) and the size of the adsorber unit. Consequently, providing sufficient bed depth and low gas velocity are important design factors.

The humidity levels, temperature and pressure during the adsorption should be monitored to maintain optimum efficiency. It should be possible to measure the performance of any adsorption equipment, ie sample points should be in place to facilitate the analysis of inflow and outflow gas streams. The adsorption equipment should be monitored for breakthrough. Similarly, other parameters such as temperature and pressure should be monitored.

Activated carbon beds can be used within the processes covered by this Note as a polishing treatment after scrubbers or LEV systems.

### 3.3.4 Cooling towers

Several types of cooling tower are in common use. These include:

- air cooling;
- natural draught cooling towers; and
- low-level mechanically assisted cooling towers.

Condensed plumes that come down to ground level can bring droplets containing biocides, or organisms that could be harmful, and can also cause loss of light, poor visibility and icing of roads. Such plumes should not be permitted.

Where plumes need to be abated the temperature and the humidity need to be controlled. This may be achieved by combining conductive heat exchange and evaporative cooling in the design of the cooling 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 the operator 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 that subtends an angle greater than 10° when viewed vertically upwards from the ground.)

An operator may propose to guarantee to reduce load or to take other appropriate action to ensure that the above conditions are met. Performance curves should be provided to enable the plume abatement to be demonstrated under a wide range of ambient conditions.

### 3.3.5. Dispersion from chimneys and vents

#### (a) Assessment and modelling

The applicant will need to demonstrate that an appropriate assessment of vent and chimney heights has been made to provide adequate dispersion of prescribed substances, and other substances that might cause harm, which cannot be prevented and may be released. Some guidance is given in Technical Guidance Note D1<sup>(9)</sup>.

For major sites it is considered BAT for dispersion modelling to be carried out, which takes into account local meteorological data, local structures and topography, as well as other local releases, to provide estimates of process contribution to ground-level concentrations of significant pollutants at appropriate production and ambient scenarios. Operators (or relevant experts acting for them) should be expected to produce and maintain an up-to-date multi-stack dispersion model for the works. Operators should provide clear information on the parameters used and the assumptions made in their use of dispersion models. Of particular relevance will be the assessment of background concentrations of pollutants and the fate in the environment of pollutants released. Statutory air quality standards<sup>(10)</sup> and other recognised criteria relating to international obligations should be taken into account.



When a significant change is being considered that could lead to an Authorisation variation, eg new plant, uprated existing plant or major feedstock quality change (outside the normal range), a new dispersion model should be presented. This should take into account the proposed changes and show the environmental impact of making them.

Where appropriate, the operator should also recognise the chimney or vent as an emergency release point. Process upsets or equipment failure giving rise to abnormally high release levels over short periods should be assessed. Even if a very low probability of occurrence can be demonstrated by the applicant, a value for the chimney or vent height should nevertheless be set to avoid any serious damage to health.

The assessments made by the operator should be validated using the appropriate calculations or dispersion models available to the Agency.

All releases must be controlled and minimised to ensure that ambient air quality beyond the process boundary complies, as a minimum, with air quality standards<sup>(10)</sup>.

### (b) Visible plume elimination

Releases from vents generally should be hot enough to avoid visible plume formation in the vicinity of the vent. This is to prevent the condensation or absorption of environmentally harmful substances by the condensing water vapour and improve dispersion. Exhaust gases from a wet scrubber can be heated by the use of waste process heat to raise the exit temperature of the exhaust gases and prevent immediate condensation on exit from the vent. This procedure increases the thermal buoyancy of the plume. Where there is no available waste heat and the vent contains no significant environmentally harmful substances, the applicant may be able to demonstrate that the BATNEEC/BPEO criteria have nonetheless been met.

### 3.3.6 Odours

Substances present in emissions to air, which are known to be odorous, should be identified and quantified (for example, ammonia has an odour threshold of 1.5 ppm and hydrogen sulphide 0.0004 ppm). Techniques described in this Note should be employed to ensure that they are minimised to prevent them being noticeable outside the site boundary.

The main methods normally used for odour control are:

- biological systems such as biofiltration/bioscrubbing;
- activated carbon;
- wet chemical scrubbing; and
- thermal/catalytic oxidation.

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

Biofiltration represents a relatively new biological treatment method for gaseous waste streams. It generally uses beds of peat/heather or other organic materials, for example, bark or some composts. Bioscrubbing on the other hand takes place in towers containing a bioflora.

## 3.4 Minimisation and treatment of releases to water

### 3.4.1 Minimisation

Waste water can arise from the process, from storm water, from cooling water, from accidental releases of raw materials, products or waste materials, and from fire-fighting. These should all be taken into account when dealing with the process Authorisation.

Aqueous wastes generated from processes in this sector may contain a wide range of species such as cyanides, sulphides, dissolved organics, suspended organics, dissolved heavy-metal compounds including sulphates and fluorides as well as suspended solids.

The characteristics of releases to water from a chemical plant largely depend upon the type of process involved, the standards of housekeeping, the degree of recycling achieved, and whether or not potential releases to air are transferred into the aqueous medium, eg by gas scrubbing.

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

- Minimise the presence of water in the process including water used in product purification and equipment cleaning.
- Use dry techniques where appropriate to abate particulate and gaseous exhaust streams.
- Rinsing processes should seek to minimise water consumption by reducing process drag-out and using appropriate techniques and technology to maximise water conservation and re-use.
- Recycle or re-use water back to the processes or to secondary uses such as equipment wash-down where possible.
- Where possible, rinse water consumption should be metered.
- Where possible, intermittent discharges or extreme variations in flow, concentration or other characteristics should be balanced before treatment.
- Employ indirect-contact heat exchange devices.
- Segregate process water, rain water and indirect cooling water streams to reduce the hydraulic loading to waste-water treatment equipment or sewers.
- Develop spill contingency procedures to minimise the risk of accidental releases of raw materials, products and waste materials and to control such spillages to prevent their entry into water.

- Shelter bunded areas to prevent transfer of contaminants to rain water with subsequent release to the environment.
- Eliminate equipment washing between batches of the same product unless essential. Where this is not possible, such as at weekend shut-down, a reduced level of cleaning should be considered.
- Use dry cleaning methods wherever practicable for solids. Vacuum extraction reduces the loss of product to water and, in some cases, allows the recovery of these products.
- Wipe down equipment that is accessible rather than washing and rinsing it.

Where appropriate, liquid effluents of different characteristics should be segregated for treatment.

Areas where spillages are most likely, such as transfer and sampling points, should drain to sumps. The sumps should be discharged to effluent treatment after the composition of the contents has been checked. Self-sealing couplings should be used where applicable.

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 drain. The Environment Agency has issued guidance on oil tank storage<sup>(16)</sup>.

Bunds should be regularly inspected for structural integrity by a competent person. Bunds not frequently inspected should be fitted with a high-level probe and an alarm as appropriate.

Contaminated rain-water accumulations should be directed to appropriate treatment.

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

Care should be taken in the choice of organic cleaners used, eg detergents, which can enter the effluent system, as they may act as complexing agents with metals and impair treatment performance.

Treatment chemicals such as corrosion inhibitors, coagulants, flocculants, descaling agents, sodium hydroxide and biocides should be chosen such that they minimise substances prescribed for water, eg mercury in sodium hydroxide.

Treatment chemicals and biocides should be stored in sealable bunded areas, or equivalent, and returned to those areas after use.

Process waters, site drainage waters and chemically contaminated waters should, where appropriate, be treated.

The dilution of aqueous process streams by mixing with general site effluent or the mixing of process streams from different

processes to achieve co-dilution is generally not considered to represent BATNEEC. An applicant wishing to use this procedure should demonstrate that it represents BPEO as opposed to applying treatment to the concentrated process stream.

### 3.4.2 Water collection

#### (a) Process waters

Process waters are those obtained as a result of the processes carried on in the chemical works and arise from specific plant items. Examples include process filtrates, distillation condensates, liquors from wet arrestment devices, vacuum pump sealing fluids and wash-down/drainage from process, handling and storage areas.

As a consequence of their direct contact with other process fluids, process waters may have become contaminated. Accordingly, they should be conveyed from source via an appropriate system to treatment plants in a closed system as far as practicable. The system should be designed to prevent leakage into ground and to prevent ingress of groundwater.

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

- waste-water streams contaminated with heavy metals;
- waste-water streams contaminated with hydrocarbons;
- waste-water streams contaminated with chlorinated hydrocarbons; and
- acidic and alkaline waste-water streams.
- Potential releases should be minimised by the following methods:
  - Vacuum lines should pass through knock-out pots and separators for recycle wherever possible.
  - The use of process fluids for liquid ring pump sealing should be considered, and the subsequent use of these contaminated streams within the process.
  - Consideration should be given to the use of dry vacuum pumps that do not use either a sealing fluid or lubricating oil.
  - Where sealing fluids are used the installation of closed systems should be considered together with heat-exchange equipment and scrubbing facilities.

#### (b) Site drainage waters

These are essentially rain water running off hard surfaced process areas and roofs or collected by purpose-designed drains.

In many cases an oil separator will be required for site drainage waters<sup>(17)</sup>.

The site drainage should be designed such that spillages of chemicals, etc, should be routed to the effluent system with

provisions to contain surges and storm-water flows.

Absorbents should be used to mop up minor leaks and spills and should be disposed of to leak-proof containers.

The collection system should also take account of the additional fire water flows (BS 5908<sup>(38)</sup> gives some guidance), or fire-fighting foams. Emergency storage lagoons may be needed to prevent contaminated fire water reaching controlled waters<sup>(39)</sup>.

### (c) Cooling waters

Discharges from once-through cooling water systems or other sources should not be used to achieve, by dilution, release limits for substances prescribed for water being discharged from treatment plants.

Cooling waters are generally used in indirect, recirculatory systems.

### 3.4.3 Treatment methods

Further information is available in Technical Guidance Note A4<sup>(40)</sup> and from the ETBPP guides<sup>(29)</sup>.

It is unlikely that any single waste-water treatment technique will be adequate to render harmless the waste water to be discharged. For example:

- A waste-water stream containing hexavalent chromium will require reduction to the trivalent form at low pH followed by precipitation at high pH.
- A waste-water stream containing cyanide and with a high pH would require cyanide destruction followed by pH adjustment.
- A waste-water 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 water from valuable metal compound manufacture (eg platinum and palladium) is treated with metal scavengers such as copper, zinc or iron to displace the valuable components, which are recovered by filtration before the waste liquor is discharged to the effluent treatment plant.

Treatment methods including combinations of (a) to (e) below should be applied as appropriate. Generally the larger the site effluent volume, the more complex the treatment system. Smaller sites (less than 40 m<sup>3</sup>/day effluent) are liable to carry out basic treatment before discharging the effluent to a sewerage undertaker.

#### (a) In-plant treatment

- For cyanides and sulphides, combinations of: air or wet oxidation; ion exchange; stripping; granular activated carbon.

- For heavy metals, combinations of: oxidation/reduction; precipitation; filtration; ion exchange; reverse osmosis; electrochemical techniques.
- For organics, combinations of: wet oxidation; ion exchange; reverse osmosis; electrodialysis.

#### (b) Primary treatment

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

- Physical water treatment systems.
- Neutralisation.
- Oxidation.
- Solids removal
  - settlement,
  - flotation,
  - precipitation,
  - dewatering,
  - filtration.

#### (c) Secondary/tertiary treatment

Secondary treatment systems can be either single systems or conjugated systems to reduce or eliminate chemical species present in the aqueous stream.

- Activated carbon adsorption.
- Ion exchange/macrocyclic resins.
- Membrane processes.
- Biological treatment.
- Electrochemical techniques
  - electro-deposition.

#### (d) Sludge dewatering

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

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

**(e) Sludge disposal**

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

- ☐ Recovery, eg primary extraction.
- ☐ Land.
- ☐ Encapsulation.
- ☐ Lagoon.
- ☐ Incinerator.

**3.4.4 Primary treatment****(a) Stripping**

Steam stripping techniques are used to remove volatile components dissolved in aqueous effluent streams. Very often gaseous effluent streams requiring further treatment can be formed. The BPEO of the stripping process should be justified in the application.

Removal of sulphur contaminants or phosphine can be achieved by steam or air stripping. This process is especially useful for stripping trace amounts of phosphine from by-product phosphoric acid and from water and sodium hydroxide scrubbing liquors.

Care should be taken when selecting construction materials, particularly for the column overhead equipment, since severe corrosion can be encountered. Contaminated effluent steam strippers are prone to plugging, and sequestering agents are frequently used to prevent calcium deposition.

**(b) Neutralisation**

Effluents should be dosed with an appropriate acid or alkali to achieve a neutral solution. pH control should be carried out in a vessel constructed of suitably resistant material. The vessel should be designed to allow sufficient retention time for dosing.

Care should be exercised when acid dosing effluent in case toxic gases are released, eg chlorine from hypochlorite solution, hydrogen sulphide from sulphides, or hydrogen cyanide from cyanides. The vent from these vessels should pass to scrubbing facilities.

Dosing systems are unable to cope with effluents of extreme pH; therefore, an intermediate facility capable of storing strongly acidic or alkaline effluents should be installed with automatic control if such effluents are likely.

The control of pH is difficult since the relationship between pH and concentration of reagent is highly non-linear. A typical titration curve favours multi-stage dosing. Automatic pH meters should be backed up by regular manual pH measurements and instruments should be calibrated frequently. New technologies/control systems are being developed to improve pH control.

The neutralisation of an acid waste with an alkaline waste should be considered if compatible streams are available.

An alternative to conventional lime and sodium hydroxide for the treatment of acidic waste streams (and for treating effluents containing metals) is the use of magnesium hydroxide suspension. It has many advantages in that it is safe and easy to handle, has natural pH buffering properties, thus reducing the likelihood of a pH excursion, and reduces sludge volumes generated. For alkaline wastes, the use of carbon dioxide has some similar advantages.

**(c) Oxidation**

Oxidation of contaminants can be achieved by the addition of a variety of reagents. For example, ozone, hydrogen peroxide and sodium hypochlorite can be used. Other schemes involve pure oxygen, UV radiation and proprietary catalyst systems.

In one system, oxidation takes place over a catalyst that activates the hypochlorite ion so that the oxidation rate of a number of species is enhanced. A wide range of odorous compounds (including ammonia and hydrogen sulphide) can be destroyed, while suppressing the formation of chlorine and chlorinated by-products.

**(d) Solids Removal**

The removal of particulate matter from effluent can be hindered by fluctuations in flow. A flow balancing facility may be required upstream of any particulate matter removal equipment.

The removal of finely divided suspended solids can be enhanced by the addition of chemical coagulants/flocculants. Similarly, these substances can aid the removal of emulsified oil and grease.

The addition and mixing of pH control chemicals and flocculants can be made, as necessary, prior to raw effluent entering the tank.

Techniques for solids removal include settlement, flotation, precipitation, dewatering and filtration.

**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.

Settlement is carried out in a clarifier. The clarifier design that is considered to be the most efficient and economical is a circular, mechanically scraped tank. However, depending on the flowrate, one or more pyramidal-type settlement tanks may be appropriate.

The applicant should have identified a suitable treatment/disposal route for the resultant sludge. The option of metal recovery should be investigated.

- Control for settlement processes should include a sludge blanket

level indicator and high-level alarm. Where scrapers are used, loss-of-motion sensors should be used.

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

### *Flotation*

An alternative to sedimentation is using either induced or dissolved-air flotation, although it is less common in the chemical industry. The required tank size is substantially reduced but more ancillary equipment is needed, making the overall capital cost higher for sites with large (more than 200 m<sup>3</sup>/day) effluent volumes.

Controlled release of pressure produces a rising blanket of micro-bubbles as the dissolved air passes out of solution. The bubbles carry suspended solids to the surface of the tank where they are removed by surface skimmers. Either circular or rectangular tanks can be employed. Retention times are typically of the order of 20–40 minutes at peak hydraulic loading (influent and recycle). Addition and mixing of pH control chemicals and flocculants can be made as necessary prior to raw effluent entering the tank.

Where volatile organic chemicals may be present, an applicant proposing to use a flotation technique should assess the impact of the release to air of any of those chemicals due to the action of aeration.

Inspectors should ensure that adequate control is in place to monitor the air supply. The skimmers on the surface can be monitored by loss-of-motion sensors.

### *Precipitation*

Chemical precipitation of dissolved heavy metals is the most common method encountered and may be accomplished by either batch or continuous treatment systems. A batch system is usually designed with two tanks, each one of sufficient volume to handle the waste generated in a specific time.

Precipitation relies on the low solubility of heavy-metal hydroxides in water and they usually precipitate as very small or colloidal particles; thus coagulating agents such as a polyelectrolyte are often added to obtain a heavier precipitate to aid efficient separation.

Precipitates may be separated by settling or filtration or a combination of both. Pressure filters, media filters or vacuum filters may be used. In some cases, in order to achieve a level of metal removal in practice that approaches the theoretical, enhancing techniques such as secondary precipitate generation or filter aid addition may be necessary.

The precipitated sludge can then be drawn off and separated solids should be dewatered to obtain a sludge that may be suitable for metal recovery. Where multi-stage precipitation is used, solids separation normally occurs between stages.

Generally the precipitate is either the metal hydroxide, sulphide or carbonate and pH is set at the optimum for maximum removal; the final effluent may require subsequent pH readjustment before release to water.

The most commonly used precipitants are calcium hydroxide slurry or sodium hydroxide solution, and the appropriate choice should be made taking account of all relevant factors including the preferential recovery of the metal value from the precipitate where this is feasible. Magnesium hydroxide suspension may offer a number of advantages, including reduced sludge volume, a natural buffer pH of 9.5 and greater cost/material effectiveness.

Hydroxide solubility varies markedly with pH and species; therefore it is important to establish the optimum pH control point for the particular waste stream. This is difficult when a number of different metal ions are present, including metals not themselves covered by this Guidance Note, as individual optima vary, for example, from pH 4.3 for ferric hydroxide to pH 9.3 for nickel(II) hydroxide. In such cases a full literature survey and a programme of test work should be undertaken. Other factors such as residence time, particle growth and choice of coagulant, if any, will also need to be investigated and justified in an application. Multi-stage precipitation may be necessary and, where used, solids separation normally occurs between stages.

Sulphide precipitation may give higher removal efficiency but it requires a high degree of control to avoid excess sulphide in the final effluent and the avoidance of hydrogen sulphide generation from sludge. It may be appropriate to use both hydroxide and sulphide in a multi-stage system at increasing pH 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, eg streams containing nickel, lead and cadmium compounds.

Hydroxide and carbonate precipitation may not be sufficient to remove metal cations in one stage, requiring further precipitation reagent or different tertiary treatment such as ion exchange for full cation removal. Precipitation reactions may be subject to interferences from complexing agents, other cations and anions present. Many alternative chemicals are available for enhancing chemical precipitation efficiency for specific species.

Co-precipitation is a technique often used for heavy-metals removal. Ferric hydroxide is often used since it naturally coagulates in water without the addition of chemical coagulants. This results in very effective agglomeration of fines and colloidal material with the heavy metals naturally adsorbing to the surface of the iron solids. Iron solids are more dense than other metal hydroxide precipitates and hence are easier to settle and remove.

### *Dewatering*

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

Mechanical dewatering in addition to or instead of gravity thickening is appropriate for many liquid wastes associated with the manufacture and use of metal compounds. This gives a dewatered solid, which may be handled more readily with less risk of spillage than a slurry.

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

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

### Filtration

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

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

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

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

Where solid impurities are removed from process liquors and become waste, their means of discharge, handling, treatment and disposal should be justified.

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

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

## 3.4.5 Secondary/tertiary systems

### (a) Activated carbon adsorption

Activated carbon columns can be used for the removal of low concentrations of metal species and to polish a final effluent to provide recyclable water. Heavy metals are removed through carbon columns. In order to avoid reduced capacity after regeneration, the carbon should be acid-washed prior to re-use. TOC (total organic carbon) can often be reduced by up to 99%.

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

When there is a small or intermittent application of PAC, the carbon is disposed of with the excess sludge. Continuous application at larger plants, however, requires regeneration of the carbon. This can be accomplished by the use of wet air oxidation (WAO).

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

### (b) Ion exchange resins/macroehticular resins

Ion exchange can be employed for the removal of undesirable anions and cations from a waste water. Cations are exchanged for hydrogen or sodium, and anions for hydroxyl ions. Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Removal of fine metal-containing particles prior to ion exchange may be necessary.

Treatment of a waste water by ion exchange involves a sequence of operating steps. The waste water is passed through the resin until breakthrough occurs. The bed is then regenerated by backwashing with water and then regenerant prior to re-use. Disposal of regenerant liquors is an important factor in minimising environmental harm. Several systems have been developed specifically to reduce the quantity of chemicals released.

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

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

Ion exchange can remove cyanide and sulphide from effluent; however, it does not destroy the cyanide and a subsequent treatment of the regeneration solutions would be required.

### (c) Membrane processes

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

Membrane processes concentrate solutions by selective filtration and usually produce a purified filtrate stream and a concentrated stream.

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

As membrane processes tend to be developed for specific effluents, the applicant should demonstrate its suitability and show that the efficiency is at least as good as and preferably better than, other available techniques.

Developments include direct cleaning membrane units, which avoid problems of fouling.

New techniques include the use of gas-filled membranes for the selective removal of components. A gas-filled membrane is a hydrophobic microporous membrane in which the pores are filled with gas. When inserted between an aqueous solution containing the volatile component and a stripping solution such as sodium hydroxide or hydrochloric acid, the volatile component will diffuse preferentially through the membrane and be absorbed by the stripping solution. This technique can be used in combination with other techniques such as ion exchange.

### (d) Biological treatment

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

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

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

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

For biological treatment the pH of the feed should be kept between 6.5 and 8.5 to ensure optimum biological activity. Consideration should be given to the effect of loss of biomass due to the introduction of toxic compounds, and a stand-by

procedure should be developed for such an event. Such a procedure may include maintaining a stock of seed inoculum.

Biological treatment of effluent containing cyanide is possible, but is generally susceptible to shock loads and requires long residence times.

Biological treatment of effluent containing sulphur compounds is possible, but is susceptible to shock load. Strict control conditions are required to prevent formation of hydrogen sulphide or mercaptans, which because of their low odour threshold could lead to odour noticeable outside the boundary of the premises.

Naturally occurring sulphate-reducing bacteria can be used to generate hydrogen sulphide, which is then sparged into waste water containing metals in order to precipitate out sulphides.

### (e) Electrochemical techniques

#### *General*

Metals can be extracted from aqueous streams by sacrificial exchange. For example, adding zinc to an aqueous solution of lead salts results in the precipitation of lead, zinc being more electropositive than lead. Another example of this method is the treatment of platinum and palladium effluents with iron scrap.

Improved removal of lead from waste liquors, compared to chemical precipitation, may be achieved by the use of iron powder in electrolytic exchange.

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

#### *Electro-deposition*

Metal cations may be electroplated onto cathode materials in electrochemical cells. In some cases the plated metal may be re-used. Cation removal efficiency is dependent on physical and chemical factors, but electro-deposition alone may not achieve total cation removal. Electrochemical cells are typically used for bulk removal from high-concentration solutions such as from drag-out tanks or spent ion exchange regenerant solutions.

New technologies are developing alternative electrode designs to improve the efficiency of recovery at lower metal concentrations in effluent streams.

## 3.5 Minimisation of waste to land

### 3.5.1 Introduction

The application for Authorisation should detail all wastes from the process that are likely to be disposed of to land.

Substances for disposal to land may include effluent treatment sludges, bag filter dust, kiln residues, organic sludges, spent catalysts, liquors, floor sweepings, dried spillages and

refractory materials. Other substances may include building materials, scrap metal, maintenance items and contaminated consumables such as packaging and spent filter bags.

Efforts should be made to reclaim raw materials and products from residues and waste prior to disposal to land in order to minimise the quantities released. Recovered dusts may be re-used in the process and sludges may be reprocessed to recover metals. An example of this is the lead carbonate or hydroxide recovered during treatment of effluent from processes manufacturing lead compounds.

Amine solutions, molecular sieves, catalysts and ion exchange resins should be regenerated on-site, where practicable, to minimise the frequency of, and amounts for, disposal. This should be compatible with good air and water pollution control. Where necessary, they should be returned to the supplier for regeneration or reclamation.

Applications should include details of the facilities for the collection and storage of solid and liquid wastes that are taken off-site for treatment and/or disposal. Procedures should be established which ensure that there is no mixing of wastes except in purpose-built equipment designed for the treatment of the wastes to make them less harmful. Such equipment will form part of the Authorised process.

Conditions should be included in the Authorisation to ensure that all substances produced by the process and disposed of to land on or away from the site should be handled, loaded and transported on-site so as to prevent spillage, dust release or the generation of odours.

Materials handling includes discharging raw materials, conveying them to process, discharging, storing and conveying the product(s) and packaging it. Equipment design should ensure that there is the minimum of dust generation and that reliance is not solely placed upon dust extraction and treatment plant.

All spillage should be cleaned up without delay and, where the consequence is likely to be environmentally significant, the plant design should be such that any spillage can be collected and prevented from entering any sewer or water course.

Wastes should be sampled and characterised, which may include a detailed analysis, at appropriate frequency to ensure that they may be accepted at the waste disposal facility and so that the relevant information can be made available to the next holder as required by the Duty of Care Regulations<sup>(4)</sup>.

### 3.5.2 Contamination of soil and groundwater

Hard surfacing should be provided in areas where accidental spillage may occur, eg beneath prime movers, in storage areas, and in loading areas. The surfacing should be impermeable to process liquors. This also applies to tank bund floors. This will facilitate recovery and clean-up operations and prevent penetration into the ground. As much of sludges as practicable should be recycled for processing (eg by filtration, centrifuging, etc), to minimise the amounts requiring disposal.

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 and thus cause a breach of the requirements of the Groundwater Directive as noted in Section 1.5.6 of this Note. 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).

In addition to sealed bunds, possible measures to reduce contamination from large storage tanks include:

- double walled tanks; and
- leak detection channels.

The 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<sup>(5)</sup>, including groundwater vulnerability and the presence of groundwater protection zones.

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.



## 4 Benchmark release levels

The release levels given are achievable by all new processes using the best available techniques described in Sections 2 and 3. They are applicable to each non-combustion point source. They should not be applied as uniform release limits, but should be assessed to take account of site-specific conditions so as to comply with the requirement to use BATNEEC and BPEO and any relevant environmental quality standards.

### 4.1 Benchmark releases to air

Benchmark release levels to air are summarised in Table 4.1 by substance and process sector

**Table 4.1 Releases to air<sup>a</sup> (mg/m<sup>3</sup>).**

Substance	Process sector							
	Ammonia	Fertilisers	HCN/H <sub>2</sub> S	P + cpds	Sb, As, etc	Cd + cpds	Hg + cpds	Cr, etc. + cpds
Ammonia	30	50 <sup>b</sup>	15		15			15
Antimony					5			
Arsenic					1			
Benzene							5	
Beryllium					0.002			
Bromine	5							
Cadmium and cpds (as Cd)						0.05		
Carbon disulphide			5	5				
Carbon monoxide			100		100			100
Chlorine			10	10	10			10
Chromium (III) <sup>c</sup>								5
Chromium (VI) <sup>d</sup>								0.5
Chromium (VI) <sup>e</sup>								1
Cyanogen chloride			1					
1,2-Dichloroethane						5		
Gaseous chlorides (as HCl)		10						
Gaseous fluorides (as HF)		10						
Hydrogen bromide	5							
Hydrogen chloride	10		10	10	10			10
Hydrogen cyanide			5					
Hydrogen fluoride	5				5			5
Hydrogen iodide	5							
Hydrogen sulphide	5	5	5	5	5	5		5
Indium					1			
Inorganic cyanide dust			5					
Lead					2			
Mercury and cpds (as Hg)							0.05	
Nickel (insoluble)								10
Nickel (soluble)								2
Organic sulphides and mercaptans (as methyl mercaptan)			2	2				
Oxides of sulphur (as SO <sub>2</sub> )	200	200	200	200	200	50		200
Oxides of nitrogen (total acid forming as NO <sub>2</sub> )	150	200	200	200	200			200
Oxides of phosphorus (as P <sub>2</sub> O <sub>5</sub> )				50				
Particulate matter	20	50 <sup>a</sup>	20 <sup>c</sup>	20	20	20	20	20

Substance	Process sector							
	Ammonia	Fertilisers	HCN/H <sub>2</sub> S	P + cpds	Sb, As, etc	Cd + cpds	Hg + cpds	Cr, etc. + cpds
Phosphine				5	1			
Phosphorus oxychloride				10				
Phosphorus pentasulphide				5				
Phosphorus trichloride				10				
Platinum (soluble)					0.002			
Platinum (insoluble)					1			
Selenium					1			
Tellurium					1			
Thallium					0.05			
VOC total Class A <sup>a</sup>	20		20	20	20	20	20	20
VOC Total Class B <sup>a</sup> (as toluene)	80		80	80	80	80	80	80

- a 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 term "expressed as" is used, a correction should be carried out using the ratio of the atomic or molecular weights of the substances as appropriate.

All releases should be essentially colourless, free from persistent trailing mist or fume and free from droplets.

Releases from the processes should not give rise to an offensive odour noticeable outside the site where the process is carried on.

For associated combustion or incineration processes, reference should be made to Guidance Notes S2 1.01<sup>(7)</sup> for large combustion plant and S2 5.01<sup>(10)</sup> for chemical waste incineration, for information relating to release levels.

- b The following levels (mg/m<sup>3</sup>) achievable in the specified parts of fertiliser production.

		Particulate matter	Ammonia
Ammonium nitrate production	Prill towers and melt granulators	15*	10
	Neutralisers/reactors	30	50
	Coolers and dryers	30	50
	Evaporators	15	50
Ammonium phosphate production		50	10

- \* Where no insoluble solids are present.

- c Chromium (III) except when combined with chromium (VI) or in a soluble nickel compound.

- d Chromium (VI) when present as calcium chromate, chromium chromate, strontium chromate or zinc chromate (including zinc potassium chromate).

- e Chromium (VI) when present as all other inorganic compounds.

- f Excluding inorganic cyanides.

- g Where possible, releases of VOCs should be individually identified.

The VOC concentration levels apply where the following total mass release rates are exceeded:

Total Class A	100 g/hr
Total Class B	5 tonnes/yr or 2 kg/h, whichever is the lower (expressed as toluene)

Releases below these mass emission rates may not be trivial, and so may still require controls and the setting of appropriate release limits.

The use of a release concentration limit is not normally appropriate in the case of a release from an air-deficient saturated vapour space such as a storage tank or process vessel. An approach based on limiting total mass released or mass per unit of production is likely to be more effective.

The term 'volatile organic compounds' includes all organic compounds released to air in the gas phase. See also Appendix 1.

## 4.2 Benchmark releases to surface water

Benchmark release levels to surface water are given in Table 4.2 by substance.

**Table 4.2 Benchmark releases to water<sup>a</sup> (mg/l).**

Substance	(mg/l)
Total hydrocarbon oil content (IR method)	1-3
Biological oxygen demand (BOD) (5 day ATU @ 20°C)	20-30
Chemical oxygen demand (COD) (2 hour)	100-150
Ammoniacal nitrogen (as N)	10-15
Suspended solids (dried at 105°C)	20-30
Cadmium (expressed as cadmium)	0.01 <sup>b</sup>
Mercury (expressed as mercury)	0.005 <sup>b</sup>

- a The levels given are ranges achievable after effluent treatment and are not release limits. They are given on the basis of flow-weighted monthly averages.

PARCOM Decision 85/1 gives limits for the release of mercury from the production of its compounds. These are 0.05 mg/effluent and 0.05 g/kg of mercury processed.

On-site effluent treatment is preferred for these processes. Where discharge to sewer is proposed, the applicant should demonstrate that this option represents BATNEEC/BPEO, taking into account:

- the substances released and their separability and degradability;
- the type of sewage treatment available;
- the security of the sewage treatment system eg with regard to storm overflow; and
- the relative performance of the available sewage treatment compared with that of the site dedicated option.

Compliance with limits imposed by the sewage undertaker does not guarantee compliance with BATNEEC/BPEO.

- b Statutory Instrument (1989) No 2286<sup>(1)</sup> gives standards for cadmium and mercury in receiving waters.

## 5 Economic considerations

### 5.1 Introduction

In determining a case the Agency must translate BATNEEC into conditions to be included in the Authorisation. The BATNEEC criterion requires that a judgement be made, balancing cost against environmental damage. The operator should have constructed a BATNEEC case after examining the range of technically feasible process and/or abatement options. BATNEEC is not concerned with the financial health or resources of a particular operator. Excessive costs are viewed in the context of the process and the industry concerned, and costs of controlling releases should not be disproportionate to the environmental benefits delivered.

In the absence of scope for efficiency savings, there are two elements to the ability of a representative operator in any industry to bear extra abatement costs. One relates to the financial resources typically available for capital expenditure, whether from cash reserves or from external sources such as loans or equity. The other depends on the extent to which costs can be passed on to customers, passed back to suppliers, or absorbed by lower returns within the industry.

The inorganic chemicals sector covers a wide range of industries with different economic backgrounds. Economic assessments of four example industries (fertilisers, lead acid battery manufacture, inorganic pigments manufacture and cadmium plating) that are covered by this Guidance Note are given below.

### 5.2 Economic assessments

#### 5.2.1 Fertiliser industry

The UK fertiliser industry consists of:

- three large overseas-owned concerns, who manufacture ammonium nitrate and blended or granulate fertilisers;
- about 20 blenders, some of whom are not covered by the Regulations;
- three granule manufacturers; and
- three liquid fertiliser manufacturers.

In the decade to end 1996, most companies suffered losses during some years. The industry is operating in a competitive and declining market. Operating profit levels were better in 1996, which was characterised by strong prices and higher demand. The bigger companies operated with higher operating returns than the smaller companies.

In 1997, the main producers saw lower margins and return on capital. Turnover also decreased over the year. The situation was expected to worsen in 1998, and some of the main companies have laid off personnel.

As a consequence, in the past decade investment has been confined to efficiency and environmental improvements.

It is likely that the industry structure will remain much the same, with the three large players and several independent producers. The expected continual decline is unlikely to encourage any new entrants into the market.

All producers are concerned by the importing of ammonium nitrate at significantly lower prices (up to 20%) than home-produced fertilisers. Much of the ammonium nitrate originates from Russia and is not subject to the same environmental requirements that prevail in the UK.

The effect of these imports from the former Soviet Union has been to depress prices. After remaining low in real terms from the mid 1980s, prices increased from 1994 to 1996 by some 20% per annum, but have declined since then to below levels achieved in early 1994.

The cheaper import issue is not expected to be resolved immediately, although the EU has acted in one case of 'dumping' from the former Soviet Union. Existing anti-dumping measures expire in 2000 and it is not known whether new provisions will be put in force.

The producers' concerns are backed by statistics, which show that the production of nitrogenous fertilisers (which comprised 54% of all fertiliser production in 1996) has been falling by 5% per annum over the last 10 years, and that, in 1996 alone, imports increased by just under 11%.

Latest forecasts for the UK show that fertiliser consumption (measured through nitrogen) will fall from 1441 kt in 1996 to 1332 kt in 2007, which represents an annual decline of 0.7%.

For all of the producers, there appears to be few opportunities for expansion given the current difficult trading conditions.

Given the tight operating conditions, it is difficult to envisage significant increases in capital expenditure that would allow for new plant. However, improvements to existing plant are expected to continue.

The ability of the firms to raise additional funds for investment will vary for each company. Although 1998 is predicted to be characterised by falling prices and tighter margins, no firm conclusion can be made about the overall capability of producers in general. It would therefore be appropriate to treat each case on its own merits, considering profitability, gearing and cashflow.

The big three companies are owned by substantial overseas concerns and their potential to source funds from within will depend on internal competing priorities, both between fertiliser divisions and between the various chemical sectors.

### 5.2.2 Lead acid batteries

The UK lead acid battery industry has concentrated from many manufacturers to three large groups, plus a few independent producers. The large groups consist of both automotive battery manufacturing companies and industrial battery manufacturing companies producing in high volumes, typically in the range of 1.5–3 million batteries per site per year.

The independent manufacturers include, for example, a low-medium-volume production of automotive batteries and a low-volume niche producer making batteries for classic cars and other lower-volume/higher-margin applications.

There is little scope for further concentration of companies, although it is likely that there will be further consolidation of manufacturing within groups onto the lowest-cost, most-productive sites in order to increase scale economies, on a European scale.

The market for lead acid batteries can be divided into three main segments:

- starter batteries (mainly for automotive applications)
  - original market,
  - after-market;
- traction batteries (manufactured as elements that are combined to produce the required battery capacity); and
- other types (eg stand-by batteries).

The automotive original market refers to sales of batteries to vehicle manufacturers for new vehicles. The estimated size of this market in the UK is 1.5 million batteries a year. This demand is satisfied by domestic manufacturers. Quality, performance and price are very important. Vehicle batteries sold into the original market meet higher specifications and command higher prices than after-market equivalents. However, the prices of original equipment batteries are continually squeezed by powerful customers, who also operate in very competitive markets, and this means that profit margins for original equipment batteries are typically less than those for after-market product.

The automotive battery after-market is highly price-competitive and quality is also important. The size of this segment is estimated to be 5.5 million per annum, and there is a relatively high level of overseas imports, particularly from countries where production factors are cheaper and health, safety and environmental requirements are lower than in the UK. After-market customers are increasing in size as smaller distributors are swallowed by the bigger players in the market. This increases their negotiating power and will tend to depress prices.

The UK car battery market is worth about £128m annually. Production and trade statistics indicate that the UK car battery market grew by 12% annually from 1993 to 1996. In 1996 UK manufacturers exported 14% of output and supplied 78% of the

UK market. The average price of UK batteries declined in real terms from 1993 to 1996. Import penetration remained fairly constant at around 22% of the value of the UK market.

The Society of the British Battery Industry (SOBAT) considers that growth is unlikely to be sustainable at these levels in the long term, considering the relatively slow increases in the UK car population, and a trend to longer battery life. Imports are increasing, helped by the currently high levels of sterling.

Traction batteries are usually manufactured as cells, which are then combined to form a battery of the required specification.

Production and trade statistics indicate the UK market for traction batteries to be worth about £190m. The UK market and UK manufacturers' sales grew respectively by 37% and 35% a year from 1993 to 1996. Imports represented 4% of the UK market in 1996. UK manufacturers exported 17% of their output in 1996.

These figures should be treated with caution – SOBAT suggests that market size and growth are considerably overstated.

Other types of lead acid battery, eg stand-by batteries, are exported from the UK in large volumes. The value of exports in 1996 was £32m, compared with imports of £2.6m. (UK manufacturers' output data are not available.)

Operating profit margins are generally low (3–4%) making low-cost, high-volume production a pre-requisite, except where a niche strategy is chosen. Return on capital is typically in the range 10–15% and is very sensitive to small increases in operating costs.

New car production within Europe is expected to continue to increase up to at least the year 2000, creating a positive outlook for UK battery manufacturers. At the same time, there will be continuing pressure from powerful customers and competitively-priced imports to reduce prices and UK manufacturing costs – especially while the value of sterling remains high. In the long term, the starter battery market segment is expected to grow at a lower rate than the 12% observed from 1993 to 1996.

The traction battery market is seen as mature. Growth in the range 2–3% a year in this sector is expected. Rates of growth in the stand-by battery market segment are expected to be higher than this.

Concentration and consolidation will allow the main producers to benefit from economies of scale and will reduce the cost of abatement measures per unit of output. Current and expected future environmental compliance requirements are not generally seen as onerous within the industry by the major players.

Medium producers (ie 100,000 to 500,000 batteries a year) that compete in the automotive after-market against imported products face the most difficult and uncertain future, and are likely to be hardest hit by health, safety and environmental requirements.

### 5.2.3 Inorganic pigments

This Guidance Note is restricted to firms primarily involved in processing of inorganic pigments based on the metals chromium, lead and cadmium.

There are about 20 companies in the UK engaged in manufacturing, mixing, blending and/or further usage of inorganic pigments. For some of the smaller companies and those involved with artists' materials, inorganic pigments are a major source of activity. However, for large conglomerates pigments represent a fraction of turnover.

The production of inorganic pigments is significantly less profitable than production of organic pigments.

Cadmium pigments are primarily used for coloration of polymers, minor usage in ceramics, glasses and glazes, 'artists' paints and high-performance paints. Although the local market is stagnant, there has been a substantial rise in exports particularly to Latin America and Asia. Pigment producers are developing new products for export in the area of high-performance and water-based coatings.

For lead pigments, legislation has restricted the use of lead-based paints in consumer products and has imposed maximum lead concentration limits in ceramic products, leading to a substantial reduction in the use of white and red lead pigments in the UK. They are still used for corrosion control on steelwork and for protection of outdoor work and in paints for road markings.

Coloured pigments in the UK have also been used for the glass, ceramics, paints and plastics industries. White and green pigments have been used for car exteriors. Artists' materials have served specific niche markets.

Cadmium- and lead-based pigments possess characteristics not available in substitutes. They have advantages in less processing time, performance criteria and cost. There are also environmental problems associated with the production of organic chemicals, and it is argued that environmental evaluation of organic pigments has been less comprehensive than of inorganic ones.

The inorganic pigment industry is mature, with the producers having been established for a long time. Abatement costs related to the installation of required equipment are high for new entries and place cost pressures on smaller firms presently in the market. However, once the equipment is in place and operating, maintenance costs were assessed by companies as affordable.

Competition comes mainly from other EU companies. In recent times, competitive pressures have been from Indian and Chinese producers.

The pigment market is price rather than quality competitive, as certain qualitative standards on health, safety and the environment have to be met.

Currently pigment producers believe that their competitive position is being undermined by the strong pound.

Most of the larger companies assessed are highly profitable, with above-average returns on sales and equity. In addition, the asset base is relatively new and the evidence from company accounts shows that additional plant and equipment has been purchased over the last two years.

The companies' cash management control is sound, with acceptable days returns for creditors and debtors. In some cases, stock turn is below average.

All of the companies have strong sources of internal funding and several are reliant on parent funds. Gearing levels are not considered to be a problem given the parent companies' own internal sources.

For the smaller companies, profits are more variable, but the balance sheet structure is strong, with low levels of liabilities.

### 5.2.4 Cadmium plating

There are approximately 20 enterprises that carry out cadmium plating in the UK. Of these, about 15 are small metal plating finishing companies with on average between 50 and 200 employees. Cadmium plating generates between 5 and 10% of their total turnover. The rest are much larger companies, eg aerospace manufacturers. For the aerospace companies, of which cadmium plating is an indispensable aspect of operations, it constitutes a minuscule proportion of turnover.

Owing to the hazardous nature of cadmium, there have been attempts to develop a close substitute for all non-safety applications. Zinc alloys and aluminium have been tried, but to date no metal comes close to cadmium's unique physical properties, which include superior anti-corrosion capabilities and high natural level of lubricity.

Nevertheless, more stringent environmental guidelines have brought about an overall reduced level of activity. In particular the EU Directives of 1991 and 1993 confine the use of cadmium plating to defence, aerospace, nuclear, mining and electrical contacts.

The amount of cadmium consumed for plating fell from 147 tonnes to 80 tonnes on last estimates in 1995.

Cadmium plating enterprises use about 7% of cadmium produced, the majority going to the battery manufacturing sector. It is an oligopolistic market, with each of the enterprises holding from 2 to 10% share each.

New entrants are unlikely in the market, due to decreasing demand and costly initial investments needed to comply with environmental standards.

The small platers analysed on their financial performance vary in terms of their profit margins and are characterised by loose cash management. Some are making losses, others are achieving low margins. The cash position is exacerbated by the

delays in debtors paying outstanding accounts and the metal companies paying suppliers. Bank overdraft is used to fund operations and use of other external debt is common. Their fixed asset base is relatively new.

The large aerospace and defence companies have faced difficult trading conditions, with losses over the last three years, but operate with better cash management and liquidity.

The very scale of these operations suggests that, once they begin to generate operating profits, they could at least earn sufficient funds for investment given their better control of cash.

### 5.3 Costs of release control techniques

The companies Authorised under this industry sector Guidance Note cover a range of different industries and different scales of operation ranging from batch pilot-plant-scale facilities through to large continuous manufacturing processes. A wide range of chemical species with differing physical, chemical and toxicological properties are stored, handled and processed, which leads to the generation of waste streams to all environmental media that vary in terms of composition, concentration and the complexity of treatment that is required.

#### 5.3.1 Particulate matter

Within the inorganic chemicals industry one of the main abatement issues commonly found is the abatement of particulate matter from gaseous streams. There are a number of alternative technologies available as described in Section 3.

The choice of suitable technology will be dependent upon technical, site-specific and economic considerations, and a number of appropriate criteria for consideration are given below:

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

In some cases gaseous streams containing particulate matter will be combined together for treatment, and in other cases it may be more appropriate to segregate individual streams for abatement.

Each of the main abatement technologies for particulate matter has advantages and disadvantages, which may preclude its use on technical considerations for any particular installation.

One of the main factors is that the efficiency of particulate abatement devices is influenced by particulate size, and typical values are shown in Table 5.1. The figures should be taken as

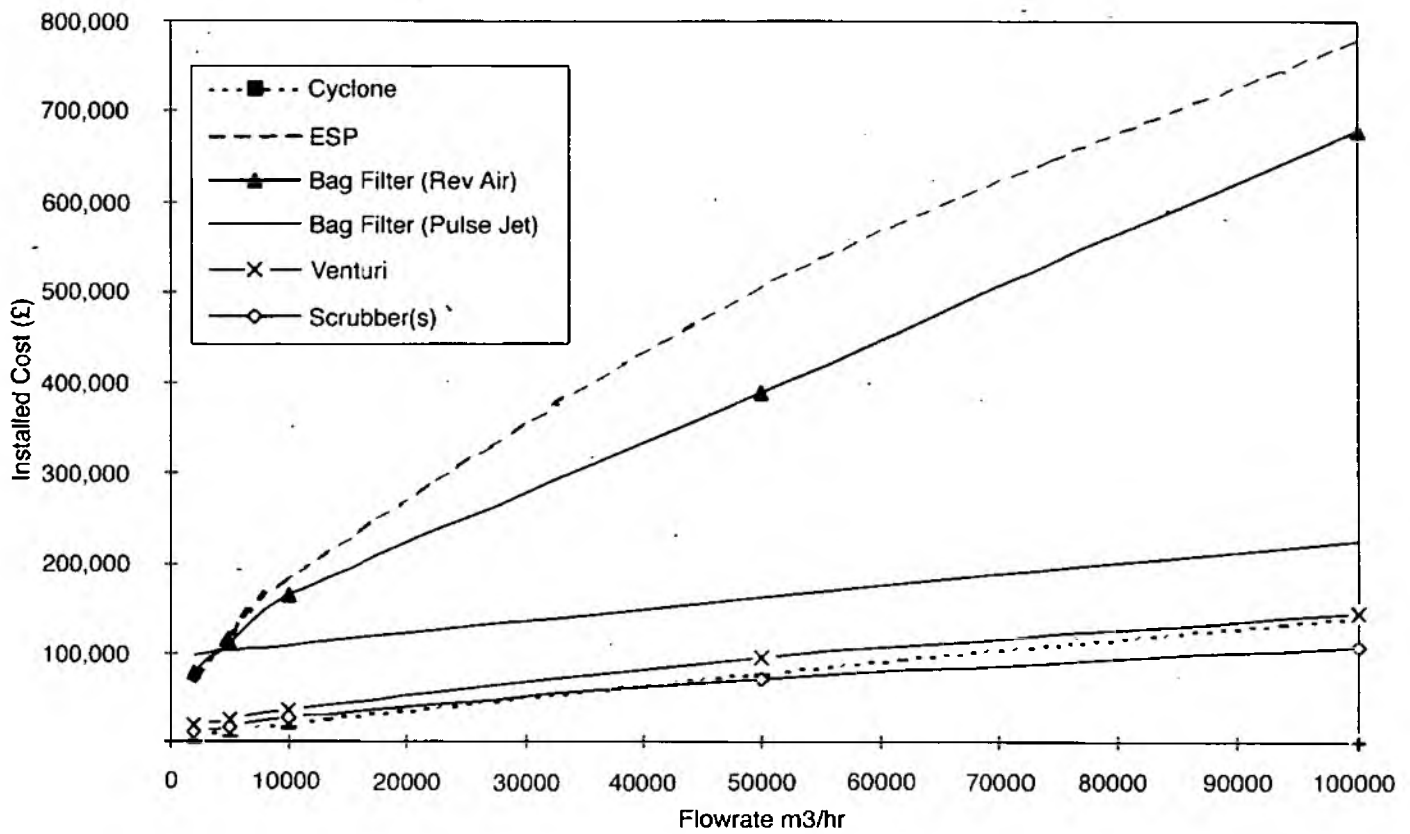
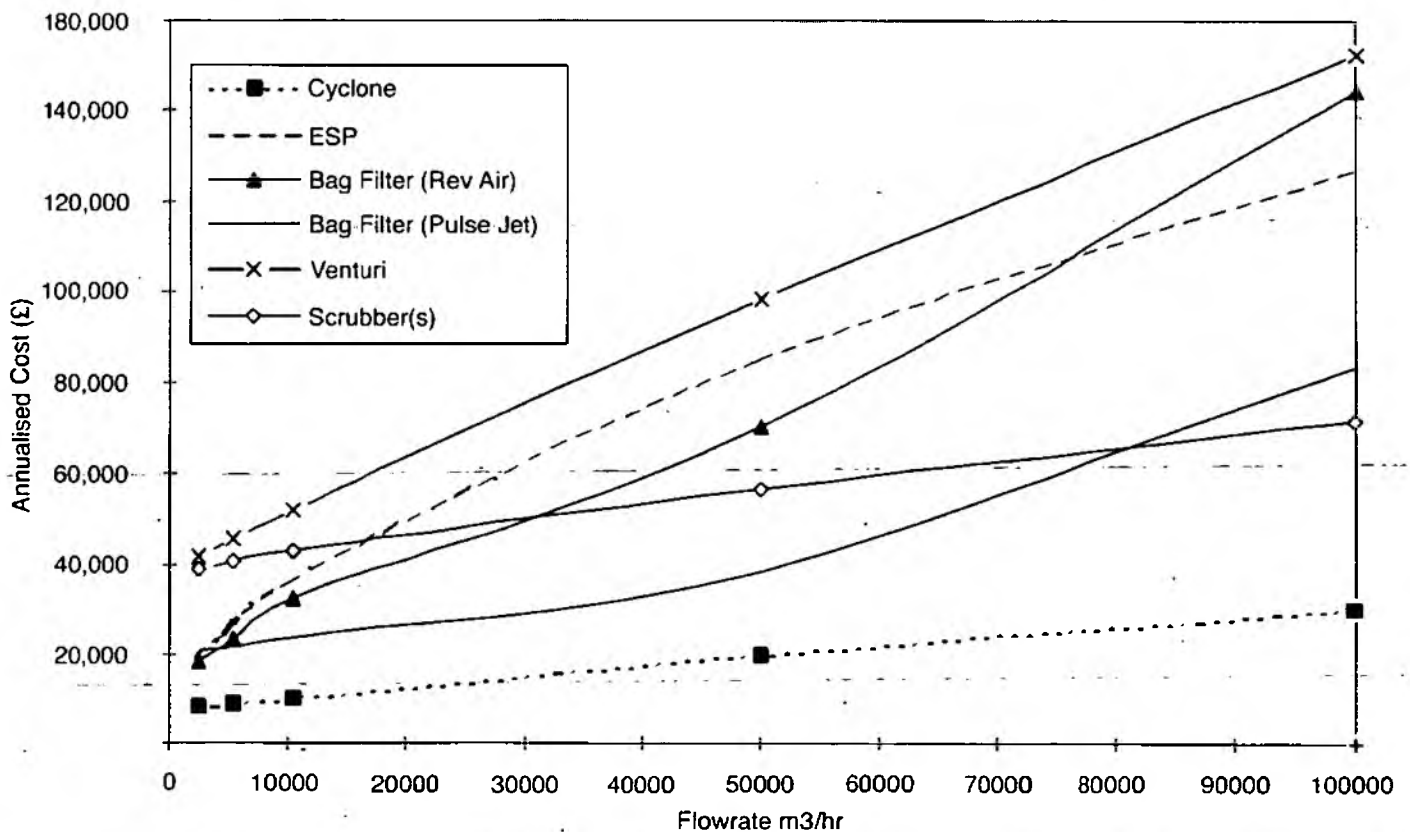
guideline values only. Actual removal efficiencies will depend on the type and density of the particulate to be removed and hence must be determined for each individual case. Combinations of treatment technologies may be required in order to achieve required emission levels.

**Table 5.1 Efficiency of particulate abatement devices.**

Type	Efficiency (%)			
	10 µm	5 µm	2 µm	1 µm
High-efficiency cyclone	87	73	46	27
Wet impingement scrubber	99.5	97	92	80
Electrostatic precipitator	99.8	99.7	99.6	99.5
Pulse jet filter	99.99	99.95	99.9	99.8

Other considerations when selecting particulate abatement systems that influence the costs include the choice of materials of construction for the plant and ancillaries such as filter bag materials of construction.

It is not possible to show comprehensive costing data to satisfy all situations and to cover all applications covered under this sector, but approximate costs of employing some of the particulate abatement control techniques discussed in this Guidance Note are given in Figures 5.1 and 5.2. They should be treated with a great deal of caution as they will vary considerably for specific applications. The data shows total installed equipment costs and annualised costs against volumetric throughput for each of the main technologies.

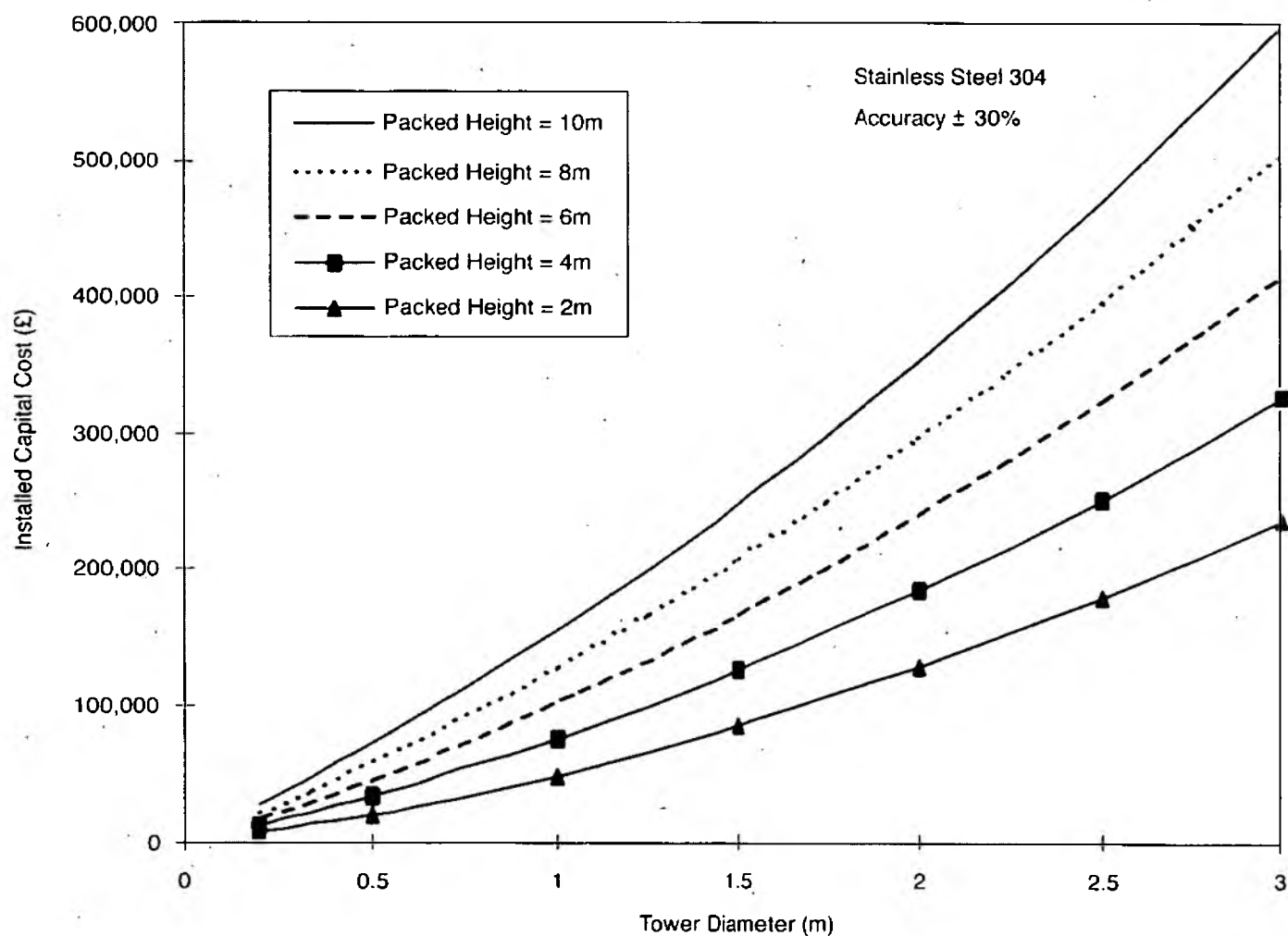
Figure 5.1 *Installed capital cost for particulate abatement equipment*Figure 5.2 *Total annualised costs for particulate abatement equipment*



### 5.3.2 Gas scrubbing

Scrubbing techniques are widely used in the sector for gaseous pollutants. However, the diverse nature of the pollutants, the scrubbing medium and operating conditions make it impracticable to give average annualised costs. Figure 5.3 shows capital costs only for a common type of scrubbing equipment constructed in stainless steel.

**Figure 5.3** *Installed cost of acid gas scrubbers*



## 6 Monitoring

### 6.1 General

There is an expanding series of HMIP and Environment Agency Technical Guidance Notes on monitoring, containing information on theory and methodology, and providing technical information on monitoring techniques (see Associated publications at the end of this Note).

Conditions in the Authorisation should require the results of all monitoring to be reported in line with the IPC standard Authorisation format.

The applicant should provide a clear statement of the potential for release of all substances that might cause harm to the environment, and propose an unambiguous set of procedures for measuring or otherwise estimating releases of key pollutants.

Information should be provided on release routes, methods of relevant monitoring or sampling and analysis, and periods and frequency of assessment. Evidence should be provided that quality assurance procedures are in place to ensure that all monitoring and test results are sufficiently accurate and reliable (for example by reference to British/international standards and accreditation with the United Kingdom Accreditation Service (UKAS)).

Reference should be made to the application when setting standards of release in Authorisations to ensure that such conditions are assessable by means described by the applicant, and are properly enforceable.

The requirements and frequency of sampling, analysis and monitoring are site- and/or process-specific, influenced by consideration of the anticipated volume and composition of the waste streams.

### 6.2 Monitoring releases to air

For continuous monitoring, release concentration levels are given on the basis of 95% of the hourly average readings for each rolling 24 hour period not exceeding the value and the maximum hourly average not exceeding 150% of the value. For non-continuous monitoring, the levels refer to the sampling period appropriate to the test method.

In order to relate emission concentrations to mass releases, it will be necessary to measure or otherwise determine the gas flow. Additionally, in order to relate measurements to reference conditions, temperature will need to be determined. Determination of oxygen or water vapour content may also be required. All such measurements should be recorded.

Where appropriate, continuous monitoring techniques should be used, commensurate with the limitations and accuracy of continuous monitors. When continuous monitoring is not appropriate or available, non-continuous monitoring should be

undertaken, together with continuous surrogate measurements where applicable.

Releases to air from kiln systems are highly variable. Continuous monitoring for particulates, SO<sub>x</sub> and NO<sub>x</sub> is particularly useful to indicate trends in plant performance.

In requiring the use of continuous monitoring for any given release point, several factors should be taken into account. These include the size of the process and its releases, the value of monitored versus calculated results (eg by using proven mass balance/factoring methods) and the usefulness of continuous records where a release may be time-dependent, such as changing over production cycles/catalyst life, etc.

The Agency has established its Monitoring Certification Scheme (MCERTS). Continuous emission monitoring systems should be expected to meet the performance standards published under the Scheme. Manual stack testing should be carried out in accordance with the separate MCERTS performance standards being developed for non-continuous monitoring, which include the use of the Agency's standard reporting formats.

Wherever a combustion process (other than flaring) is used for the destruction of a pollutant, its effectiveness should be demonstrated indirectly by continuously monitoring the temperature and oxygen content of the exhaust gas. Visual and olfactory assessments of releases from incinerators, flares, furnaces and other sources liable to cause a nuisance emission should be made when appropriate, particularly during upset/start-up/shut-down conditions. Remedial action should be taken immediately in the case of adverse observations, and the cause of the release and action taken should be recorded in the log book.

Monitoring should be undertaken during commissioning, start-up, normal operation and shut-down unless the Inspector agrees that it would be inappropriate to do so.

Where Inspectors are not satisfied with the amount of information available about emissions, a short-term monitoring exercise may be appropriate as part of an improvement programme.

### 6.3 Monitoring releases to surface water

Continuous monitoring and flow proportional sampling for releases to water are always preferable, but the use of a fixed-interval or time proportional sampler for flowrates of less than 1 litre per second may be acceptable. Spot sampling may be used for audit or enforcement purposes.

Monitoring of process effluents released to controlled waters and sewers will commonly be made for the following:

- flowrate;
- pH;
- temperature; and
- TOC (surrogate for COD/BOD).

Samples should also be monitored for appropriate other parameters such as those below, over relevant time periods, typically daily, weekly or monthly depending on circumstances:

- COD;
- hydrocarbon oil;
- ammoniacal and total nitrogen;
- suspended solids;
- phenols;
- sulphide;
- dissolved oxygen (where justified by nature of receiving water); and
- ⊕ metals (typically Cd, Hg, Cr, Ni, Zn, Cu, As).

In addition to the regular monitoring carried out by the operator to demonstrate compliance with the release limits set, the operator should have a fuller analysis carried out covering a broad spectrum of substances to establish that all relevant substances have been taken into account when setting the release limits.

Where Inspectors need to obtain more understanding of the performance of an effluent treatment plant (ETP), a short-term monitoring exercise to provide information about inputs to the ETP may be appropriate as part of an improvement programme.

#### 6.4 Monitoring releases to land

The applicant should record and advise the Agency of the quantity and composition (including prescribed substances) of waste released to land. In addition, the applicant should have written procedures which ensure that releases are handled, treated and disposed of in an approved manner, and specify how the accumulation and storage of waste are controlled.

The frequency of analysis of the waste is site- and/or process-specific, influenced by considerations of the anticipated quantity, its frequency of despatch from the site, physical form, containment (for transport) and composition. Applicants should be aware that the Agency will wish to be satisfied that analyses should be sufficient to ensure that wastes are acceptable under the terms of the Waste Management Licence of the facility where they are to be disposed of and fulfil the waste description requirements of the Duty of Care.

#### 6.5 Environmental monitoring

The impact of the process on the environment will be affected by the quantity and form of the releases, and by the site's location. Inspectors should assess the extent to which process releases have been rendered harmless and decide whether environmental monitoring will be necessary.

For major sites it is considered BAT that some form of environmental monitoring is carried out for releases to air, primarily to confirm compliance with air quality standards, but also to confirm environmental dispersion modelling. Inspectors should require operators to propose monitoring that is appropriate for the quantity and form of the releases and for the site's location. Such programmes typically commence with the use of a suitably designed grid of passive diffusion adsorption tube sampling sites. The technique provides an economical method of identifying any environmental 'hot spots' and screening to determine whether additional, more accurate and elaborate methods may be required.

#### 6.6 Groundwater impact

Where on-site disposals are made, or where there are discharges to groundwater, either directly or indirectly, the requirements of the Groundwater Directive for 'prior investigation' of the potential effects on groundwater and 'requisite surveillance' need to be addressed. The form that these will take will depend on circumstances, but it may be appropriate to include a structured programme of groundwater monitoring, eg using borehole monitoring.

In addition, where there is reason to suspect that leakage of chemicals to ground may have occurred or may be occurring, a programme of investigations should be instigated and preferably agreed with the Agency (some activities may require the Agency's prior consent).

For many sites it will be appropriate to incorporate a programme of background monitoring of groundwater to ascertain whether the process has given rise through time to groundwater contamination via leaking pipes, accidental spills, contaminated run-off, etc. This is over and above any monitoring required to monitor the effects of specific on-site disposals of solids or liquids on groundwater. Owing to the lengthy residence time and differing modes of transport and degradation in the underground environment, such monitoring is likely to be long-term and should be adapted to the types of contaminant that could be present in the potential discharges. It is essential to include background monitoring of groundwater that has not been affected by site processes (normally up-gradient in the hydraulic sense) to determine objectively the degree of contamination that may be attributable to site processes.

In setting out a programme of investigations, and when interpreting the results, operators should take account of the specific risks to groundwater and seek advice from the Agency in cases of uncertainty.

#### 6.7 Records and reporting

Inspectors shall have regard to the instructions on:

- reporting and monitoring, and
- ⊕ records and notifications related to incidents,

given with the IPC standard Authorisation format.

# Appendix 1 Volatile organic compounds

## A1.1 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.

## A1.2 Categorisation

In order to enable Inspectors properly to assess applications 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<sup>(4)</sup>, 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 prescribed substances whose release must be prevented or minimised. These are allocated to Class B.

The definition of "harm" given in the Environmental Protection Act 1990 includes offence to any of man's senses. 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)<sup>(5)</sup> 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, Inspectors should 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<sup>(6)</sup>, the Montreal Protocol<sup>(4)</sup> and Sax's *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.

## A1.3 Achievable benchmark levels

The levels of emission that can be achieved are dependent on factors that include the prescribed process itself, the VOC concerned and the abatement method used. Before abatement equipment is considered, the operator should review the process to determine whether the emission can be reduced by changes in equipment or operating conditions. It may also be possible to substitute with a less harmful or less volatile compound.

Where possible, process- and substance-specific achievable levels of release are given in Table 4.1 of this Note.

A BPEO/BATNEEC assessment<sup>(7)</sup> should be made wherever possible to determine an acceptable release level. However, in the absence of sufficient information or where it is agreed by the Inspector that an assessment is not possible, the following guidelines may be used to provide a practical approach to setting limits. Inspectors should also consider all relevant information contained in applications and other appropriate sources when they set VOC emission concentration or mass limits in Authorisations.

- 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 toluene)	2 kg/h

Releases 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 4.1 of this Note.

- For Class A compounds, state-of-the-art abatement techniques can achieve a benchmark release level of 20 mg/m<sup>3</sup> for continuous releases. Her Majesty's Inspectorate of Pollution published two Technical Guidance Notes<sup>(35,46)</sup> on pollution abatement technology, which give relevant information on such techniques.
- 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. Toluene has been used as a reference material as it is a common Class B solvent. If levels were expressed as total organic carbon (TOC), the mass concentration limit, particularly for halogenated compounds, would be too lax, as the compound may have a high molecular weight relative to its number of carbon atoms.

The Class B benchmark level has been set at 80 mg/m<sup>3</sup> toluene based on abatement techniques involving adsorption with activated carbon.

The benchmark release level for a Class B substance may be determined by multiplying the molecular weight of the pollutant by a factor of 0.87 to give the release level in mg/m<sup>3</sup>.

For mixed streams the release level may be calculated by summing the class limits multiplied by their respective mass fractions.

- The above is for guidance on setting release levels only and not for monitoring those releases. Monitoring would be expected to be for individual substance or for TOC.

HMIP Technical Guidance Note M2<sup>(3)</sup> gives more information on monitoring techniques.

- 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 effective. Reference may be made to relevant IPC Guidance Notes for Waste Disposal and Recycling (see *Associated Publications* in this Note), and the release emission concentrations used should take into account the harmfulness of the products that are released.

# References

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- 11 The Air Quality Regulations 1997. SI 1997 No 3043
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- 28 Air Pollution Advisory and Review Group, Air and Environmental Quality Division, DETR, Ashdown House, 123 Victoria Street, London SW1E 6DE
- 29 The Environmental Technology Best Practice Programme, ETSU, Harwell, Oxfordshire, OX11 0RA  
Helpline 0800 585794  
  
Good Practice Guides (relevant section)  
  
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- 38 BS 5908: 1990 *Code of Practice for fire precautions in the chemical and allied industries*
- 39 *Pollution Prevention Measures for the Control of Spillages and Fire Fighting Run-off*. PPG18. Environment Agency  
  
CIRIA Report No 164, *Design of Containment Systems for the Prevention of Water Pollution from Industrial Incidents*
- 40 *Effluent Treatment Techniques*. Technical Guidance Note (Abatement) A4. (HMSO) January 1997, ISBN 0-11-310127-9
- 41 *The Collection and Disposal of Waste Regulations 1988*. SI No 819. ISBN 0-11-086819-6  
  
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*The Controlled Waste Regulations 1992*. SI No 588. ISBN 0-11-023588-6  
  
*The Environmental Protection (Duty of Care) Regulations 1991*. SI No 2839. ISBN 011-015-8539  
  
*Waste Management, The Duty of Care, A Code of Practice*. HMSO, ISBN 0-11-752557-X  
  
*The Controlled Waste (Registration of Waste Carriers and Seizure of Vehicles) Regulations 1991*. SI No 1624. ISBN 011-014-6247
- 42 *Montreal Protocol on Substances that Deplete the Ozone Layer*. CM283. HMSO. ISBN 0-10-102832-6
- 44 *The Categorisation of Volatile Organic Compounds*. Research Report No DOE/HMIP/RR/95/009, available from the Environment Agency's Public Enquiries Unit, Rio House, Waterside Drive, Aztec West, Bristol BS12 4UD
- 45 *CHIP, The Chemicals (Hazard Information and Packaging) Regulations Approved Supply List*. (TSO) ISBN 0-11-882156-3
- 46 *Technical Guidance Note (Abatement) A2. Pollution Abatement Technology for the Reduction of Solvent Vapour Emissions*. (HMSO) January 1997, ISBN 0-11-310127-9

# Abbreviations and definitions of terms used

BAT	Best Available Technique(s)	HTS	High temperature shift
BATNEEC	Best Available Technique(s) Not Entailing Excessive Cost	IPC	Integrated Pollution Control
BOD	Biological oxygen demand	IPCGN	IPC Guidance Note
BPEO	Best Practicable Environmental Option	LDAR	Leak detection and repair
CCA	Copper chrome arsenic	LEC	Liquid-encapsulated Czochralski
CFCs	Chlorofluorocarbons	LTS	Low temperature shift
CHP	Combined heat and power	MDEA	Methyldiethanolamine
CIGN	Chief Inspector's Guidance Note	MOCVD	Metal oxide chemical vapour deposition
CIMAH	Control of Industrial Major Accident Hazards	MOVPE	Metal oxide vapour-phase epitaxy
CO	Carbon monoxide	NaHS	Sodium hydrogen sulphide
COD	Chemical oxygen demand	NAMAS	National Measurement Accreditation Service
EA	Environment Agency	NH <sub>3</sub>	Ammonia
EC	European Community	NO <sub>2</sub>	Nitrogen dioxide
EDTA	Ethylenediamine tetraacetic acid	NO <sub>x</sub>	A mixture of nitric oxide and nitrogen dioxide
EP	Electrostatic precipitator	NPK	Nitrogen, phosphorus, potassium
EPAQS	Expert Panel on Air Quality Standards	NTA	Nitrilotriacetic acid
EPA90	The Environmental Protection Act 1990	PAC	Powdered activated carbon
ESP	Electrostatic precipitator	PSA	Pressure swing adsorption
ETBPP	Environmental Technology Best Practice Programme	PVC	Polyvinyl chloride
ETP	Effluent treatment plant	TSO	Stationery Office
GAC	Granular activated carbon	SO <sub>x</sub>	A mixture of sulphur dioxide and sulphur trioxide
HCFCs	Hydrochlorofluorocarbons	SRU	Sulphur recovery unit
HCN	Hydrogen cyanide	SSP	Single superphosphate
HEPA	High-efficiency particulate arrestment	SVL	Strong VAT liquor
Hg	Mercury	SWS	Sour water stripping
HHV	High heat value	TGN	Technical Guidance Note
HMIP	Her Majesty's Inspectorate of Pollution	TOC	Total organic carbon
H <sub>2</sub> S	Hydrogen sulphide	tpd	tonnes per day
HSE	Health and Safety Executive	UKAS	UK Accreditation Service
		VOC	Volatile organic compound



## Associated publications

The following are available from Stationery Office bookshops (see back cover), their accredited agents, and some larger bookshops.

### Series 2

**Chief Inspector's Guidance Notes (prepared by Her Majesty's Inspectorate of Pollution)**

**Fuel production processes, combustion processes (including power generation)**

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S2 1.03 Combustion processes: compression ignition engines 50 MW(th) and over

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**Supersedes IPR 1/3**

S2 1.04 Combustion processes: waste and recovered oil burners 3 MW(th) and over

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**Supersedes IPR 1/4**

S2 1.05 Combustion processes: combustion of fuel manufactured from or comprised of solid waste in appliances 3 MW(th) and over

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**Supersedes IPR 1/5 1/8**

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E1 Best practicable environmental option assessments for Integrated Pollution Control  
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## Relevant DETR publications

*Integrated Pollution Control: a practical guide.*  
(HMSO) £5.00, ISBN 0-11-752750-5


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