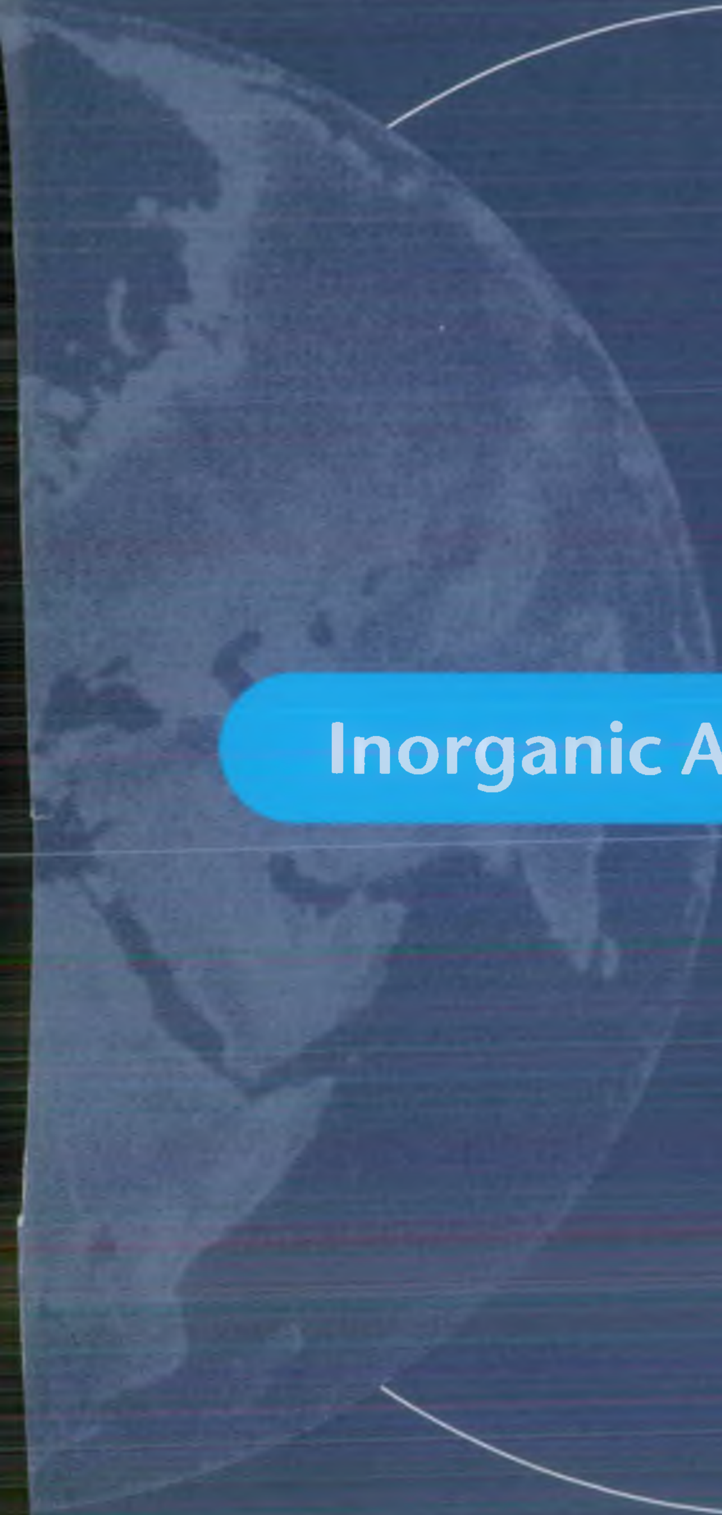
Technical
Guidance

IPC S2 4.03

ENVIRONMENT
AGENCY



Process Guidance

Inorganic Acids and Halogens

Enquiries about the contents of this publication should be made to:

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Processes Subject to Integrated Pollution Control

IPC Guidance Note
Series 2 (S2)
Chemical Industry Sector

S2 4.03: Inorganic Acids and Halogens

Prepared by the Environment Agency 1999

London: The Stationery Office Ltd

Publishing organisation
Environment Agency
Rio House
Waterside Drive
Aztec West
Almondsbury
Bristol BS32 4UD

Tel 01454 624400
Fax 01454 624409

ISBN 0 11 310141 4

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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 acid and halogen manufacture and processes related to them. It supersedes Her Majesty's Inspectorate of Pollution's Chief Inspector's Guidance Notes IPR 4/10, IPR 4/11, IPR 4/13 and IPR 4/14 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 4.3 and 4.4 of the Regulations. Other inorganic chemical processes prescribed for IPC are covered by IPC Guidance Note S2 4.04.

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 the relevant sectors of the chemical industry is included.

Contents

1 Introduction

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 4/10, 4/11, 4/13 and 4/14 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(1) 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(2), in assessing operators' proposals relating to their Authorisations under EPA90. This Note should be used together with separate guidance on monitoring(3), dispersion methodology(4), and assessment principles for determining Best Available Techniques Not Entailing Excessive Cost (BATNEEC) and the Best Practicable Environmental Option (BPEO)(5,6) 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:

- O description(s) of the principal processes covered by the Note;
- O the prescribed substances and other substances that can cause harm and are most likely to be released from the processes;
- O guidance on best available techniques (BATs) for the control of releases;
- O benchmark achievable release levels;
- O other environmental standards relevant to the process; and
- O 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 Combatting of Air Pollution from Industrial Plants known as the Air Framework Directive (84/360/EEC)(7). Article 13 requires the following points to be taken into account:

- O the plant's technical characteristics;
- O its rate of utilisation and remaining life;
- O the nature and volume of polluting emissions from it; and
- O 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 releases 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 acids, halogens and related processes. Most, but not all, are continuous and relate most closely to those listed in Sections 4.3 and 4.4 of the Regulations(1).

The main process are:

- O sulphuric acid production;
- O nitric acid production;
- O halogens, halides and oxyhalogens; and
- O titanium dioxide by the sulphate and chloride routes.

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.

Other inorganic chemical processes are covered by IPC Guidance Note S2 4.04(8).

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(3) for more information.

Releases may be expressed in terms of mg/m^3, 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(9) gives limit values in air for the following substances:

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

1.5.2 Air quality objectives

Statutory Instrument 1997 No 3043, *Environmental Protection, The Air Quality Regulations* 1997(10) gives air quality objectives to be achieved by 2005 for:

- benzene;
- 1,3–butadiene;
- carbon monoxide;
- lead;
- nitrogen dioxide;
- PM$_{10}$; and
- sulphur dioxide.

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

1.5.3 Water quality objectives

Statutory Instrument (1989) No 2286(11), *The Surface Waters (Dangerous Substances Classification) Regulations* gives the annual mean concentration limit values for certain substances in receiving waters. These include cadmium and mercury.

1.5.4 The UNECE Convention on Long-Range Transboundary Air Pollution(12)

Under this Convention, a requirement further to reduce SO$_2$ emissions from all sources has been agreed. The second Sulphur Protocol (Oslo, 1994) obliges the UK to reduce SO$_2$ emissions by 80% (based on 1980 levels) by 2010. Negotiations are now under way which could lead to a requirement further to reduce emissions of NO$_x$ and volatile organic compounds (VOCs).

1.5.5 Volatile organic compounds

'Reducing Emissions of VOCs and Levels of Ground Level Ozone: A UK Strategy'(13) 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.

EC Directive 90/415/EEC(14) covers releases to water from the production and use of 1,2-dichloroethane, trichloroethylene, perchloroethylene and trichlorobenzene.

1.5.6 Mercury and chlorine

PARCOM Decision 90/3 relates(15) to the reduction of atmospheric emissions from chlor-alkali plants.

EC Directive 82/176/EEC(16) gives release limits for mercury from chlor-alkali plants to water.

1.5.7 Titanium dioxide

EC Directive 92/112/EEC(17) covers waste from the manufacture of titanium dioxide.

1.5.8 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'(18). 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)(19) 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(18). 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 makes 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 of 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:

- **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 major processes are briefly described and the release routes of pollutants are indicated. The control techniques considered to be BAT for each process are described in this section, where they are special to the process, or are covered in Section 3 (general techniques).

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 Sulphuric acid

2.2.1 Manufacture of sulphuric acid from sulphur

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

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

The sulphur dioxide feed can originate from a variety of sources, including smelting processes, but the proportion of sulphur dioxide produced in the UK from elemental sulphur is over 90%.

Some sulphuric acid is produced from spent sulphuric acid, either by decomposition and regeneration or by concentration in multi-effect evaporators.

(a) Process chemistry

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

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

$$S + O_2 \rightarrow SO_2 \qquad (1)$$
$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad (2)$$
$$SO_3 + H_2O \rightleftharpoons H_2SO_4 \qquad (3)$$

The combustion reaction (1) is irreversible. The ignition temperature of pure sulphur is about 260°C; however an optimum temperature for the reaction would be around 1000°C. This temperature is too high for the conversion of sulphur dioxide to sulphur trioxide and so the gas stream is cooled before it enters the converter.

Oxidation of the sulphur dioxide (2) is a reversible reaction and occurs at an appreciable rate in the forward direction only at temperatures above 380°C in the presence of a suitable vanadium pentoxide catalyst. Reaction temperatures are generally between 380 and 620°C. The equilibrium of the reaction is influenced by temperature, inlet gas SO_2 concentration and the ratio of oxygen to sulphur dioxide. Maintaining the correct ratio is essential for obtaining maximum conversion.

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

(b) Process description -- single absorption

The single absorption process is illustrated in Figure 2.1.

Water vapour in the process air to the plant is removed in a drying tower circulating concentrated (96–98%) sulphuric acid. The pressure is boosted to between 0.35 and 0.70 barg by the main blower. The dry air is fed to the sulphur furnace where liquid sulphur is sprayed and burnt to form sulphur dioxide. Drying is essential to minimise acid mist formation, as, otherwise, SO_3 will react with the water vapour to produce very fine acid droplets (<10 µm).

A waste heat boiler is normally used to cool the furnace exhaust gases from about 1000°C to the required converter inlet temperature of between 400 and 500°C.

The converter normally consists of four catalytic beds in which the sulphur dioxide is oxidised to sulphur trioxide. Heat of reaction has to be removed after each stage so that the process gas re-enters the converter between 400 and 500°C. Sometimes, temperature control is effected by the staged introduction of air between the beds of the converter.

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

The conversion efficiency depends on the inlet gas composition and the operating temperatures within the converter. For a single absorption sulphur-burning plant the typical conversion efficiency is in the range 98 to 98.5%. This performance is readily achievable when there is steady-state operation and with an O_2:SO_2 ratio of about 1.3-1.6 (ie 8–9% SO_2) in the feed gas.

The process equilibrium is such that conversion improves on reduction of the inlet gas strength. On some plants, additional "dilution" air is added to the gas entering the second and subsequent stages of the converter.

Single absorption processes tend to be favoured where SO_2 concentrations are lower and for more variable, eg metallurgical SO_2. They are also utilised in older existing plant.

(c) Process description – double absorption

The process is similar to that of single absorption except that after the second or third catalytic stage the gas is cooled and passed to an intermediate absorber which extracts the sulphur trioxide that has been formed (see Figure 2.2).

Sulphur-trioxide-free gas is then returned to the subsequent stages of the reactor. This results in increased total sulphur dioxide oxidation when compared to the single absorption process. The 98% product acid is generated in the intermediate

Figure 2.1 ***Sulphuric acid from sulphur – single absorption***

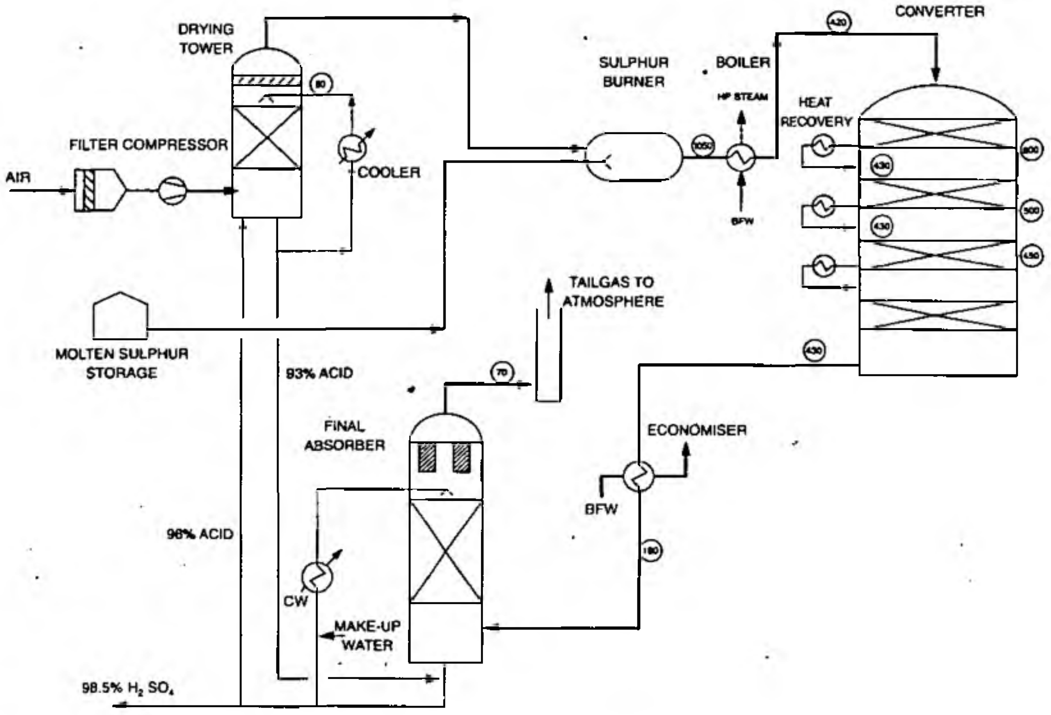
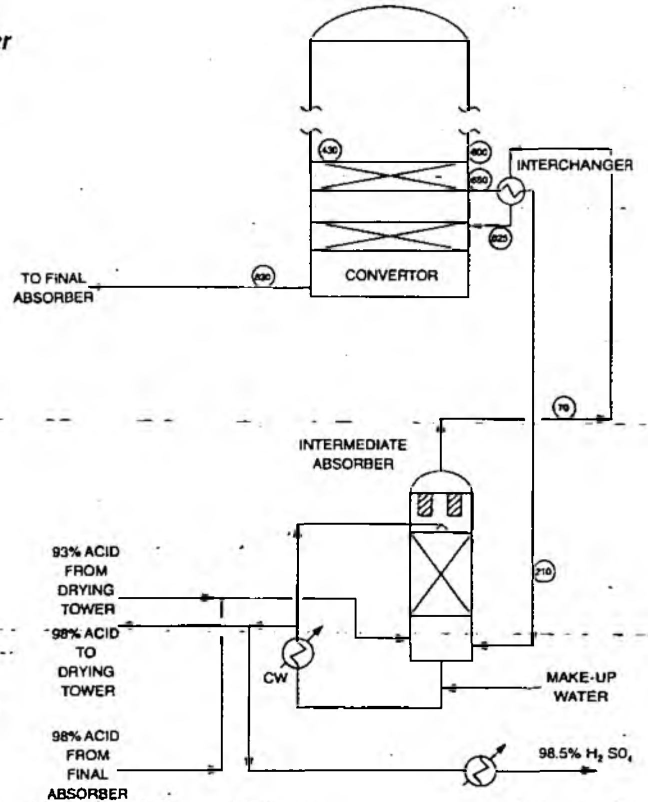


Figure 2.2 ***Intermediate absorber***



absorber where the SO_3 absorption is greatest. The final absorber also produces 98% acid, which is recycled to the intermediate absorber. If a 93% acid product is required, this may be taken from the final absorber acid loop.

Acid/water balances need to be carefully controlled between the dryer, intermediate absorber and final absorber. Flexibility of operation is usually accommodated within the acid circuit.

The double absorption process was developed to give conversion efficiencies over 99.5% and therefore much reduced sulphur dioxide outlet concentrations *and hence releases to air*. It can operate with an O_2:SO_2 ratio of 1.0 (ie 10.5% SO_2 in the feed gas on a sulphur-burning plant).

For new sulphuric acid plant, double absorption burning sulphur at steady state is the preferred technique.

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

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

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

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

(d) Combustion of sulphur

Sulphur storage and handling

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

Sulphur recovered from oil refining processes will contain significant levels of hydrogen sulphide; in this case a closed ventilation system fitted with a caustic scrubber should be used.

Molten sulphur lines and spray nozzles should be steam-jacketed to hold the sulphur temperature within the range 120–140°C.

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

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

Sulphur furnace

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

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

At high flame temperatures, small amounts of NO_x may be formed. The furnace exhaust gases are usually cooled rapidly in the downstream waste heat boiler, thereby minimising decomposition of the nitrogen oxides. There is a tendency for the NO_x to accumulate in the acid that is collected in the mist eliminators downstream of the final sulphur trioxide absorber.

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

(e) Catalytic converter

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

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

Commercially available catalysts are based on vanadium pentoxide as the active agent and promote the reaction at temperatures between 400 and 620°C. 'Low bite' catalysts containing caesium and other alkali metals have a lower ignition temperature of about 380°C. They provide the potential for increased overall efficiency and hence lower SO_2 releases to air, albeit at higher cost, by shifting the equilibrium towards SO_3 (low-temperature effect).

Preheating

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

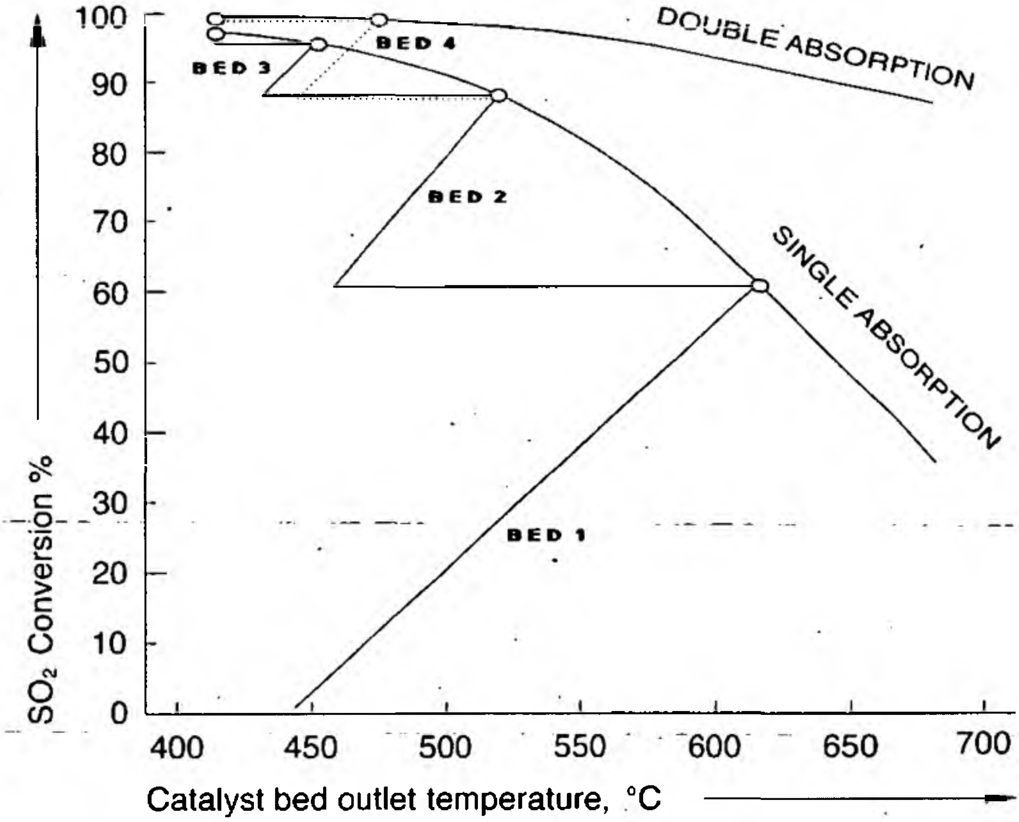
The catalyst beds in the converter may be preheated directly with combustion gases from the burning of oil, or indirectly with hot (usually dried) air from oil- or gas-fired preheaters, or a combination of both techniques.

The aim is to have as many of the four catalyst beds at temperatures at which the catalyst will 'strike' before SO_2 is admitted. While the optimum arrangement will vary between plants, it is unlikely that a satisfactory start-up will result if fewer than two beds can 'strike' immediately and the third and fourth beds are more than 100°C below 'strike' temperature beforehand. If the catalyst does not 'strike' on admission of SO_2, the feed must be stopped promptly.

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

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

Figure 2.3 ***Comparison of single absorption and double absorption processes***



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

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

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

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

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

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

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

Converter temperatures

It is possible, as a matter of routine, to maintain very steady conditions when operating a sulphur-burning sulphuric acid plant.

Back-up thermocouples should be provided, and the temperatures within the catalyst mass should also be recorded. Regular calibration checks should be carried out and faulty thermocouples replaced as part of the ongoing maintenance programme.

If good records are maintained, it is possible to detect the gradual but inevitable deterioration in the condition of the catalyst in the first pass. It is normal practice for the catalyst in the first pass to be sieved every two years and typically there is a need for top-up with new material. The spent catalyst is either removed by the catalyst supplier for recycling or sent to a landfill site for disposal.

(f) Feed conditions

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

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

The plant should be fitted with safety interlocks that prevent continued operation upon equipment failure, eg the sulphur feed pump is tripped on reduction or loss of the main airflow. This should be detected through measurement of the airflow itself instead of indirectly such as through a 'motor failed' signal.

(g) Sulphur trioxide absorption

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

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

Mist formation in absorption towers

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

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

Any droplets entrained in the gas stream at the top of the absorption towers are large, ie 10–100 µm and easy to collect in a mesh-type separator. However, acid mist is an aerosol of fine drops of sulphuric acid with particle sizes ranging from 10 µm down to 0.07 µm and is, therefore, very difficult to collect.

The mist is formed either by condensation of sulphuric acid vapour as the gas is cooled or by reaction between sulphur trioxide gas and water vapour at a temperature at which sulphuric acid can condense.

Mist formed before the absorption tower passes unchanged through the tower and will pass through a similar packed tower even if irrigated with an alkali. Any aqueous medium makes more mist due to the presence of sulphur trioxide and acid vapour.

Mist collection equipment

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

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

Until comparatively recently, more attention had been devoted to the prevention of mist formation than to its removal, but filters are now available to remove practically all forms of acid mist.

The candle-type filter is an effective filtration device and it is now widely used in the industry. The high efficiency of the candle-type filter relies either on impact or on the effects of Brownian motion.

Candle filters are increasingly used in both absorbers on a double absorption plant to ensure an invisible plume and reduce damage to the plant.

(h) Circulating acid system

The operation of absorption and drying towers is closely linked (see Figure 2.1) and forms the 'acid system', of which there are two types.

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

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

The drying and absorption towers are packed towers and the acid circulation rates are set to limit the temperature rise of the acid. Heat of absorption is removed in acid coolers, examples of which include anodically protected shell and tube exchangers, plate-type coolers with Hastelloy C plates, spiral heat exchangers, and Teflon coolers with small-bore tubes.

The double acid system is more complex in design and operation than its single counterpart. Separating the acid streams keeps them independent of each other. This enables control of acid strengths and temperatures and allows greater flexibility on complete plant and product control especially during plant start-up.

(i) Tail gas treatment

There are several viable methods for clean-up and reduction of SO_2 content in the tail gas from the absorber. Some have developed specific to the sulphuric acid industry; others have been used in the desulphurisation of flue gas from power stations. Processes can also be classified as regenerative or non-regenerative.

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

Processes that are available commercially include:

- activated carbon processes that produce dilute sulphuric acid;
- oxidation of SO_2 to SO_3 (and sulphuric acid) by hydrogen peroxide;

- solvent absorption processes with recovery of SO_2 during regeneration of solvent; and
- desulphurisation processes.

Activated carbon processes

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

Hydrogen peroxide treatment

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

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

The process was primarily designed for low SO_2 concentrations, eg exit gas from a double absorption process, as the oxidant is expensive in terms of operational costs.

Scrubbing processes

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

Solvents in use include:

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

Essentially all the processes function in a similar way and involve an absorption/scrubbing stage followed by a regeneration stage in which the SO_2 is recovered and, where practicable, the solvent is regenerated.

Efficiency of SO_2 removal for these processes can be better than 95%.

These 'add–on' processes offer the prospect of being a simpler and cheaper cost than conversion to double absorption, whilst producing a potentially saleable product or by-product. Of these processes, the hydrogen peroxide process is likely to have the lowest capital cost, but highest operating cost due to the price of H_2O_2. In addition, they may be useful in single or double absorption processes during plant start-up situations to mitigate high SO_2 losses. In such situations the H_2O_2 process may be acceptable.

Gas Desulphurisation

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

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

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

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

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

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

Processes that produce a useful by-product such as gypsum or ammonium sulphate should be required to show that a market can be foreseen for that product.

In particular the quantity of gypsum produced by abating sulphuric acid plant emissions is substantially less than from coal-burning power stations. Hence it may be uneconomic to find outlets.

(j) Pressure process

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

One potential method of reducing the level of sulphur dioxide emission lies in being able to operate the last stage of conversion in a separate reactor vessel operating at an elevated pressure of 150 kPa(g). A compressor is required to boost the gas through the reactor and associated absorber but a tail gas expander allows 80% energy recovery. This process is potentially a cheaper method of achieving low sulphur dioxide emissions than tail gas scrubbing, but it is understood that the technology has not yet been proven on a production plant. Inspectors should be aware that such techniques are being developed.

(k) Potential release routes

Releases to air

- Sulphur dioxide and sulphur trioxide from absorption column.
- Carbon dioxide from combustion plant.
- Nitrogen oxides from absorber column.
- Hydrogen sulphide, from sulphur storage.

Releases to water

- Effluent from absorption column mist collection equipment.

Releases to land

- Spent vanadium pentoxide (and alkali-metal sulphates) catalyst.
- Spent and contaminated sulphur and sulphur filter cake.

2.2.2 Manufacture of sulphuric acid from smelters and roasters

(a) Introduction

Primary smelting operations that extract non-ferrous metals from sulphide ores result in the emission of exhaust gases containing sulphur dioxide.

Such plants need to be provided with 'SO_2 abatement systems' and the sulphur dioxide concentration is often sufficiently high for this pollution control facility to consist of a conventional sulphuric acid plant located downstream of the various items of gas cleaning equipment.

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

(b) Process description

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

Metallurgical off-gases will include:

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

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

As a result of the need for extensive clean-up, the feed gas is cold (40°C) compared with over 1000°C (before quenching) from virgin sulphuric acid plants. The exothermic heat of reaction is therefore used to heat up the incoming gas. Energy may not be available for export.

Contact plants cease to be autothermal when the sulphur dioxide concentration in the converter feed gas falls below approximately 4.5%. The exact point at which this occurs depends on the amount of heat exchange surface area available.

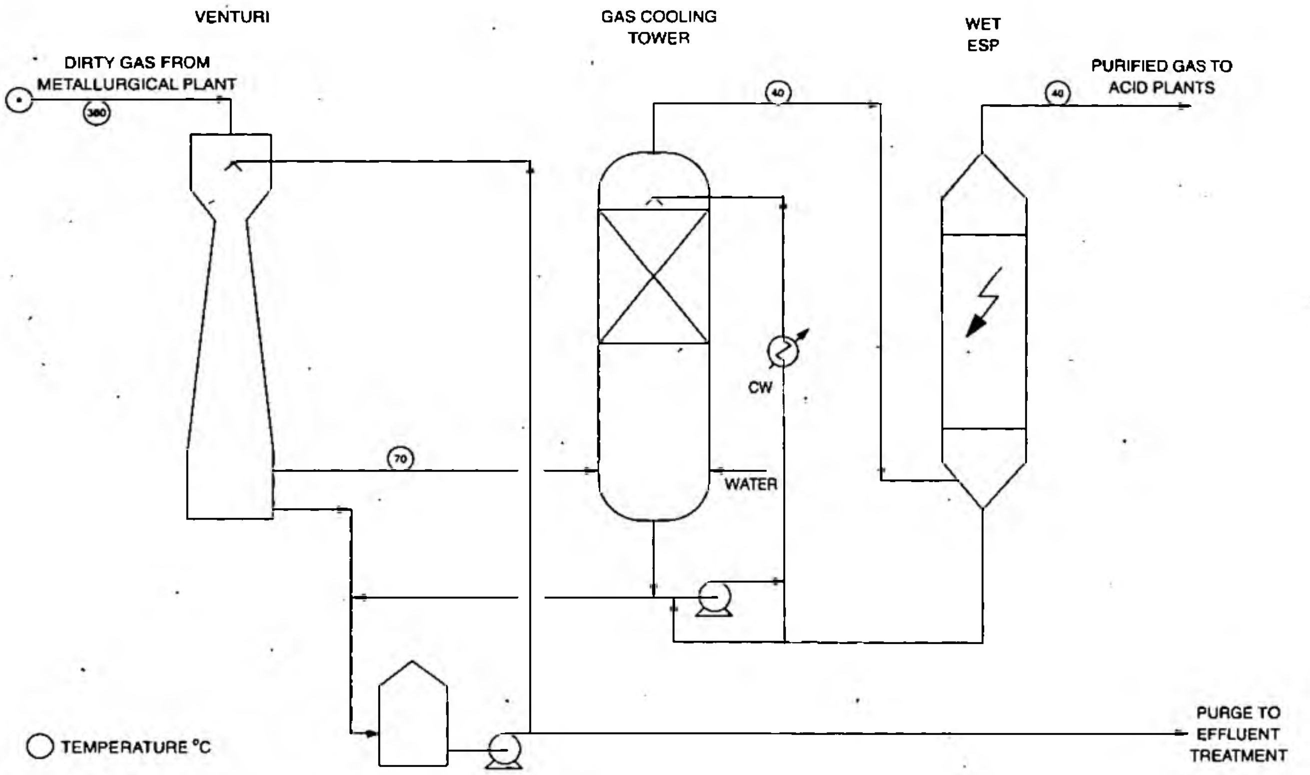
The feed gas to the contact section can have a widely fluctuating SO_2 concentration and flowrate that often falls below that required to sustain the reactions in the contact plant.

Lower concentrations of SO_2 (down to 2%) may be best treated using the single absorption process as more heat is available for heating the cold feed. Also the single-absorption-process is less sensitive to variations in SO_2 concentrations.

Plant operation must be carefully controlled to ensure that, whenever there is a requirement for top-up heat, the heater is quickly brought into service before the temperatures in the reactor fall below the 'strike' temperature of the catalyst.

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

Figure 2.4 *Typical flow scheme for gas clean-up*



The initial dust collection may be achieved in a variable throat venturi scrubber or a dry electrostatic precipitator; see Section 3.

Nickel ores may contain traces of selenium that pass into the exhaust gas as selenium dioxide, which is subsequently removed in the gas scrubber. The selenium compounds can be precipitated from the scrubber liquor bleed stream by arranging for a settling tank to be held at weakly acidic conditions of pH 4 to 5.

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

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

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

Each of the electrostatic precipitators in the gas cleaning train is normally fitted with a water seal that should be covered. These seals 'break' in the event of over-suction, thereby drawing ambient air into the plant and thus preventing any release of sulphur dioxide. There is effectively no danger of 'blowing' the seals through overpressure. As an additional precaution there should be means to establish the integrity of the seal.

Some mist is formed in the gas purification section, as the small quantity of sulphur trioxide present in the furnace or roaster exhaust gases reacts with water vapour.

Once this mist is formed, it is very stable and difficult to collect. High-efficiency lead tube electrostatic precipitators can be used for this duty, and it is becoming common practice to provide a two-stage collection system so that some collection is maintained even when one precipitator is out of service. An efficiency of 98.5% can be achieved with a single unit.

The usual criterion of satisfactory mist precipitator performance is that the outlet gas, when viewed through the sight glass provided, is optically clear, corresponding to an outlet loading of about 30 mg of SO_3 per m^3.

Operating experience suggests that mist collection is improved if the temperature at the inlet of the primary precipitators is sufficiently above ambient (40°C is a good temperature at which to run if the plant water balance permits this). The mist particles, which act as condensation nuclei, become significantly enlarged as water vapour condenses out of the gas stream.

(c) Acid bleaching

Acid produced from sinter gas can contain hydrocarbons carried forward in the gas stream from the sinter plant. This carbonaceous material causes the acid to be dark in colour and reduces its commercial value. This coloration can be removed by 'bleaching' the concentrated acid with hydrogen peroxide solution. The proportion of peroxide used varies with the initial colour but is of the order of 2 kg H_2O_2 per tonne 96.5% sulphuric acid produced. The economics of the process are such that the feed acid should be free of SO_2 to prevent the gas mopping up the expensive peroxide.

The continuous process involves the intimate mixing of the acid and the peroxide through a nozzle. Retention time in the bleaching tanks is a few hours. Increasing the temperature of the reaction greatly enhances the bleaching but at the cost of increased peroxide decomposition. The bleaching process evolves carbon dioxide and some oxygen. Careful control of the hydrogen peroxide injection is required to avoid any excess, which could corrode downstream pipework. Sulphur dioxide injection is allowed for to reduce any excess.

(d) Potential release routes

Releases to air

- Sulphur dioxide and sulphur trioxide from absorption column.
- Carbon dioxide from combustion and bleaching plant.

Releases to water

- Gas clean-up produces contaminated water, which requires treatment, before consented discharge.

Releases to land

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

2.2.3 Manufacture of oleum and sulphur trioxide

(a) Manufacture of oleum

Oleum, or fuming sulphuric acid, is sulphuric acid containing sulphur trioxide in excess over the formula H_2SO_4, eg 20% oleum contains 20% sulphur trioxide and 80% sulphuric acid.

Oleum is normally manufactured with SO_3 free weight concentrations of either 20% or 65%. The freezing points of these products are -15°C and 0°C respectively.

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

Sulphur trioxide is absorbed in a circulating stream of oleum whose concentration is controlled by cross-bleeding sulphuric acid from the acid circulation system. Sulphur trioxide absorption is limited by its vapour pressure above the oleum. The remaining 30–60% is subsequently removed in the downstream absorber on the acid plant.

Vents and overflow pipework on liquid SO_3 and strong (>35%) oleum storage tanks should not pass directly to atmosphere but should be vented to an adequate SO_3 absorber system, such as a packed tower irrigated with 98% H_2SO_4. High-level alarms and overflow protection arrangements must be designed to prevent external spillage, fume emission and moisture ingress.

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

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

For liquid SO_3 and oleums with a high vapour pressure, storage vents must be maintained at a temperature sufficient to prevent condensation and solidification of SO_3. In practice this requires steam tracing or high-integrity electric tracing to be installed and lagged to a high standard, such that all piping and fittings are maintained at 80°C. Temperature, pressure and current (for electric tracing) monitoring or data-logging are recommended, with a trace heating failure alarm.

(b) Manufacture of liquid sulphur trioxide

Liquid sulphur trioxide is produced by distilling oleum to drive off gaseous sulphur trioxide, which is then condensed. The reduced-strength oleum can either be used as a product or be returned to the oleum absorber for further sulphur trioxide addition and re-use.

(c) Potential release routes

These release routes include those for the contact process for the manufacture of sulphuric acid where applicable.

Releases to air

- Sulphur dioxide and sulphur trioxide from absorption column.
- Carbon dioxide from combustion plant.

Releases to water

- Effluent from absorption column mist collection equipment.

Releases to land

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

2.2.4 Manufacture of liquid sulphur dioxide

(a) Introduction

Liquid sulphur dioxide is manufactured by the following two methods:

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

(b) Partial condensation

The partial condensation method for producing liquid sulphur dioxide is a pollution-free process which operates in association with a sulphuric acid plant.

The plant inlet gas is a side stream from the sulphur-doxide-rich gas stream that forms the feed gas stream to a sulphuric acid plant. This is taken from downstream of the waste heat boiler after the sulphur furnace, or after the drying tower on a wet gas plant.

The gas is first cooled against the plant tail gas, after which it is filtered to remove any traces of sulphuric acid mist that may have been formed in the drying tower. Cooling down to about - 65°C results in the condensation of much of the sulphur dioxide.

The residual gas from the sulphur dioxide liquefier contains a significant concentration of sulphur dioxide and should therefore be returned to the sulphuric acid plant and added to the converter inlet gas.

(c) Potential release routes for condensation process

None.

(d) Reaction of sulphur trioxide with liquid sulphur

This method is more complex than compression-liquefaction. However, it does have the advantage that a very pure product is made and there is not the same compression and cooling requirement. The process is normally integrated with the operation of a concentrated sulphuric acid plant producing oleum that is described in Section 2.2.3.

Molten sulphur is fed continuously with a stoichiometric amount of liquid sulphur trioxide into an agitated reactor containing hot oleum. The heat of reaction is removed by either cooling coils or jacket circulating water at ambient temperature.

The sulphur dioxide produced is fed through a bed containing solid sulphur to reduce any gaseous sulphur trioxide. Any residual SO_3 is removed in a 98% sulphuric acid absorber. The pure SO_2 gas stream is condensed and stored in a vessel that maintains the pressure for the entire process.

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

Any sulphur trioxide vents can be returned to any of the absorption towers on the sulphuric acid plant while any sulphur dioxide vents can be fed to the converter inlet.

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

(e) Potential release routes for reaction process

Releases to air

- Release of sulphur oxides upon draining reactor contents.

Releases to water

- Spent reactor contents.
- Sulphuric acid effluent from reactor off-gas purification.

Releases to land

- Dirty excess sulphur settled out of spent reactor contents.

2.2.5 Decomposition of spent sulphuric acid and its recovery

(a) Introduction

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

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

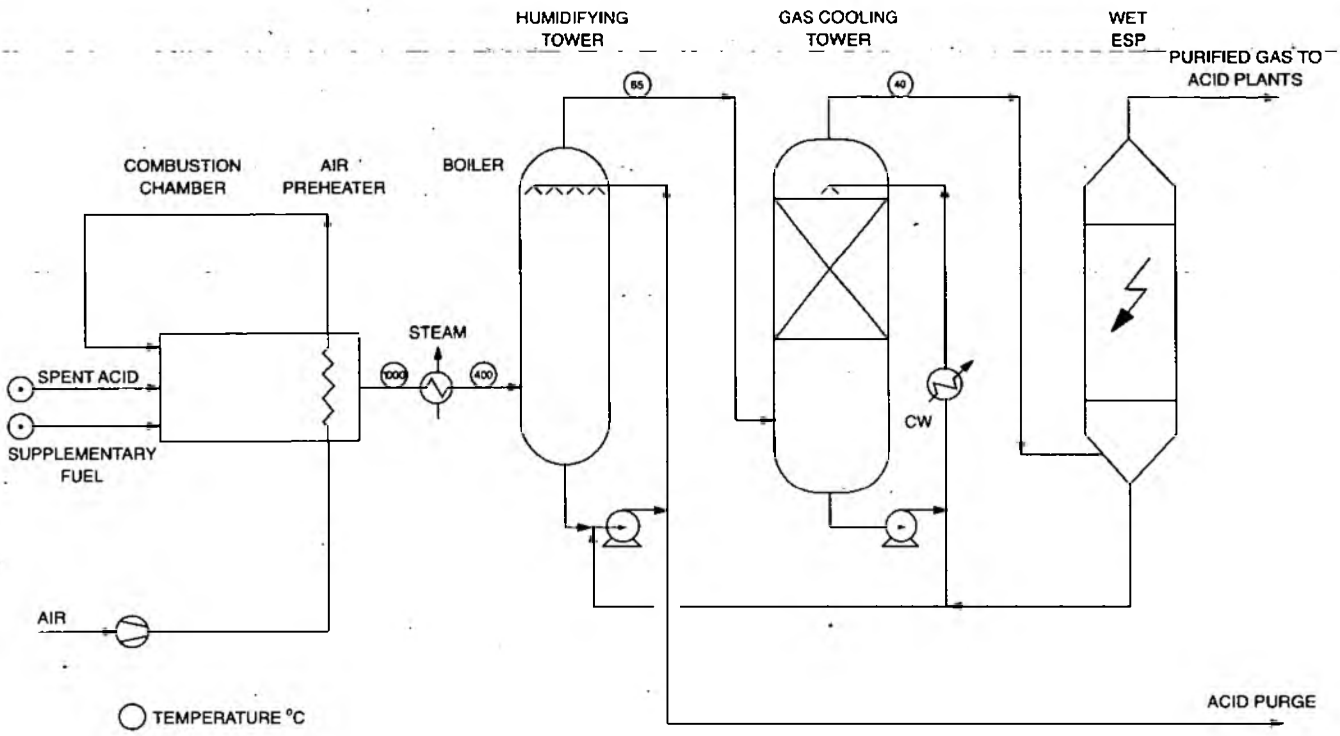
Typical sources of spent acid are from:

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

(b) Process description

The organic content of the acid is effectively incinerated as part of the decomposition process. Unless there is sufficient organic

Figure 2.5 ***Spent acid decomposition and clean-up***



material present in the spent acid, additional fuel is required. The energy required for decomposition may be provided by oil or gas. Liquid sulphur or hydrogen sulphide may also be fed to the furnace if the required acid production rate exceeds that of the spent acid.

A typical combustion scheme is shown in Figure 2.5.

Below about 2% free oxygen there is a possibility that some sulphur dioxide will be reduced to sulphur, which can sublime onto walls and the baffle plate at the back end of the furnace. Besides potential blockage problems, subsequent ignition of this material would result in uncontrolled combustion conditions and fire damage. Too high a free oxygen content, while making the plant easier to operate, increases the equilibrium value and therefore formation of sulphur trioxide in the furnace.

The combustion process operates at about 1000°C and requires cooling to about 350 – 400°C for purification.

A waste heat boiler recovers heat from the furnace exhaust gases, which then pass to the purification section.

The combustion gases include undecomposed SO_3, particulates and surplus water vapour, all of which must be removed to obtain a high–quality acid product.

The sulphur trioxide is collected as acid mist in the scrubber/precipitator section and, although recovery and re-use may be possible, is usually lost in the effluent. Under normal operating conditions 1–1.5% of the feed acid is lost in this way.

The bleed from the circulating acid stream around the scrubbing tower is one of the liquid effluents from the process. Its flow is adjusted to maintain a designed acid concentration.

Saturated gas leaving the top of the scrubber is cooled either directly or indirectly to reduce the water vapour content of the gas to the drying tower, thereby ensuring the correct plant water balance.

If oleum is being produced in the contact plant, there will be an increased gas cooling duty and a possible need for refrigerated water in the gas coolers. Condensate is often routed back through the scrubber to make up for the purge required to prevent build–up of solids. The condensed water leaves the plant as a weakly acidic liquid effluent stream.

An electrostatic precipitator is used to remove the last traces of sulphuric acid mist. The purified sulphur dioxide is then converted to sulphur trioxide, which is absorbed in sulphuric acid to produce more concentrated sulphuric acid. This can be done by either the single or double absorption process as described above.

One process variant is to use oxygen instead of air for the combustion process in the furnace. The furnace is designed to operate at temperatures similar to those in conventional sulphuric acid plant and the exhaust gases contain sulphur dioxide. The use of oxygen reduces the gas volumes by a factor of 2, but apart from the use of much smaller equipment the plant is essentially the same as that described above. Dilution air is bled into the plant at the drying tower so that the concentration of sulphur dioxide in the feed gas to the converter will be at the normal level of 11%. The absence of atmospheric nitrogen during combustion also ensures that nitrogen oxides are not formed.

The water content of the spent acid is critical to the design and operation of the plant. More dilute acids require extra supplementary fuel firing, and hence greater quantities of combustion gases (reducing the SO_2 content). Below 65–70 wt% H_2SO_4, the SO_2 content (less than about 3%) is insufficient to sustain autothermal operation of the converter in the acid plant. Strategies to overcome this include:

- preconcentration of the spent acid;
- use of oxygen or oxygen-enriched air;
- refrigeration of the off--gases to condense more water; and
- preheating of air to 450–600°C.

On failure of the acid plant main blower the feeds to the spent acid decomposition furnace should be tripped to prevent the uncontrolled emissions of sulphur dioxide from the furnace.

(c) Potential release routes

These potential release routes include those for the contact process for manufacture of sulphuric acid, as detailed in Section 2.2.1(k), where applicable.

Releases to air

- Sulphur dioxide and sulphur trioxide from absorption column.
- Carbon dioxide from combustion plant.
- Volatile organic compounds.

Releases to water

- Effluent from absorption column mist collection equipment.
- Acid effluent from gas purification section.

Releases to land

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

2.2.6 Recovery of sulphuric acid from nitration processes

(a) Introduction

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

The diluted or 'spent' acid, which is typically at a concentration of 70–72%, can be concentrated up to 91–93% for re-use.

Any impurities that are introduced into the acid are such that they are either eliminated with the evaporated water or are not deleterious if they remain in the product acid.

Whatever process is used to recover the spent acid, heat must be supplied to:

- evaporate the water; and
- raise the acid temperature.

This process operation can be achieved in either a vacuum concentrator or a drum concentrator.

The process of concentration is suitable for spent acids containing:

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

(b) Vacuum concentration

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

The acid is first preheated and then passed into a rectification column where the organic contaminants are stripped out of the acid. A small amount of pre-concentration also takes place and the acid is fed to the first-stage evaporator.

The temperature of outlet acid from the stripping column is raised to approximately 5°C above the acid boiling point at the operating vacuum. When the jet of acid enters the vessel, flash evaporation occurs. Any small droplets of acid that are entrained in the overhead vapour streams deposit on the pipework and run back into the evaporators.

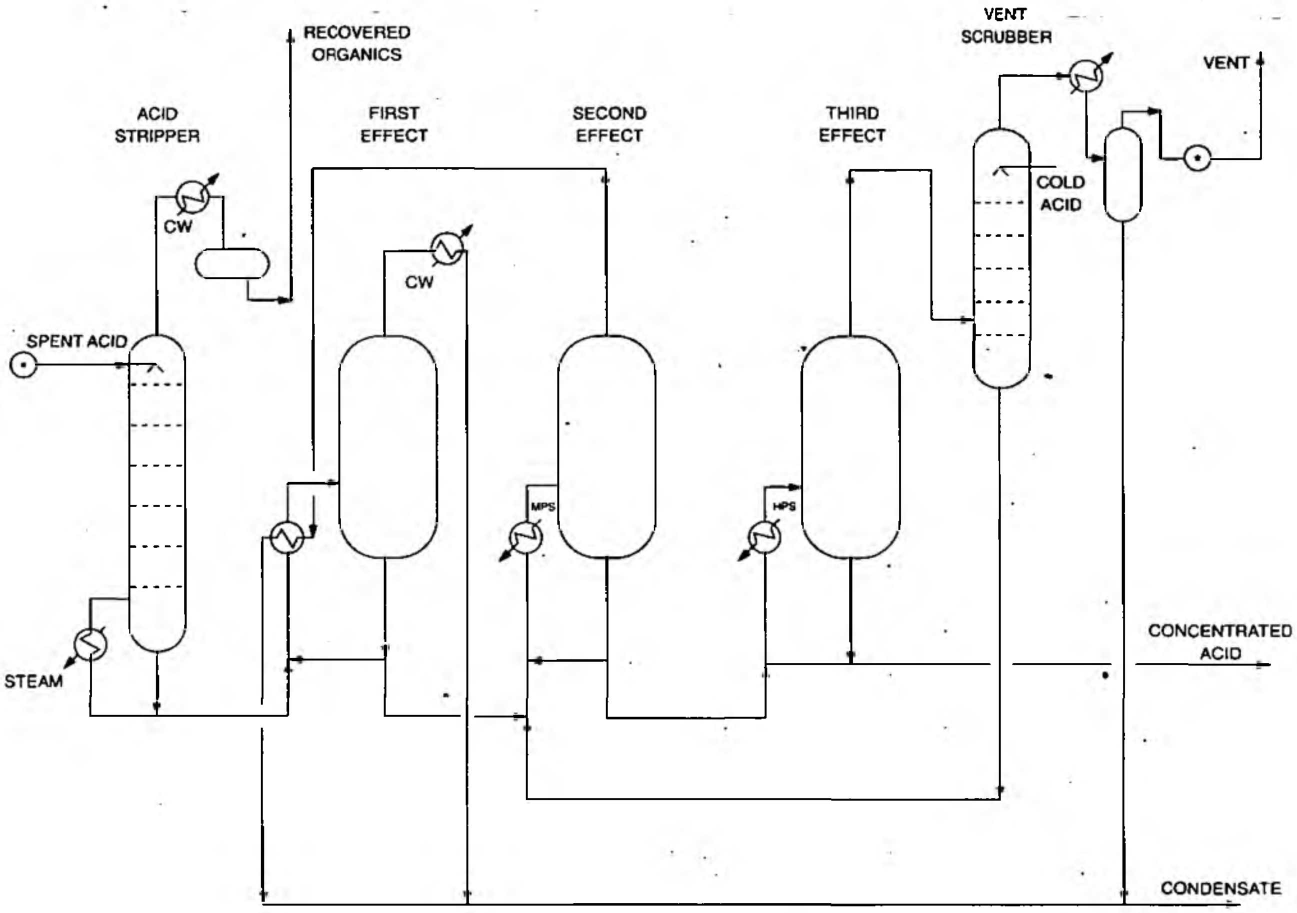
A typical evaporation scheme is shown in Figure 2.6.

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

Steam is normally used in the acid heaters and there is a water-cooled condenser for the collection of the water vapour evaporated from the acid.

The overhead vapour streams from the evaporator vessels and the steam ejector are collected into a common duct, cooled and

Figure 2.6 ***Multi-effect evaporation***



condensed under a barometric seal. Contaminated condensate is an acidic effluent from the plant and requires neutralisation.

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

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

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

Effluent treatment is required to complete the oxidation of organics to CO_2 and hence achieve acceptable biological/chemical oxygen demend (BOD/COD) levels, eliminate odorous materials and achieve satisfactory aqueous stream discharge quality.

Spent acid concentration may be effective in removing up to 97% or more of the organic material from the recovered acid.

(c) Drum concentration

This plant consists of three vessels in series, in which the acid, flowing through each in turn in one direction, is contacted directly with hot combustion gas at 750°C from a furnace flowing counter-currently.

The interconnected vessels are known as the high-, intermediate- and low-stage drums and are lined with lead and bricks. The high-stage drum contacts the combustion gas first and operates at the highest temperature, and therefore the highest concentration.

The hot combustion gas is bubbled below the acid surface through silicon–iron dip pipes. Exhaust gas from the low-stage drum is scrubbed and then discharged to atmosphere through a discharge stack.

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

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

(d) Potential release routes

Releases to air

- Sulphur dioxide and sulphur trioxide from absorption column.
- Uncondensed gaseous effluent from concentrator scrubbers containing nitrogen monoxide, nitrogen dioxide and volatile organic compounds.
- Carbon dioxide from combustion plant.

Releases to water

- Acidic effluent containing benzene and nitrobenzene from concentrator scrubbers.

Releases to land

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

2.2.7 Processes using sulphuric acid or releasing sulphur compounds

(a) Manufacture of titanium dioxide

Introduction

There are principally two commercial processes for the manufacture of titanium dioxide (TiO_2), both of which are the subject of an EC Directive(17).

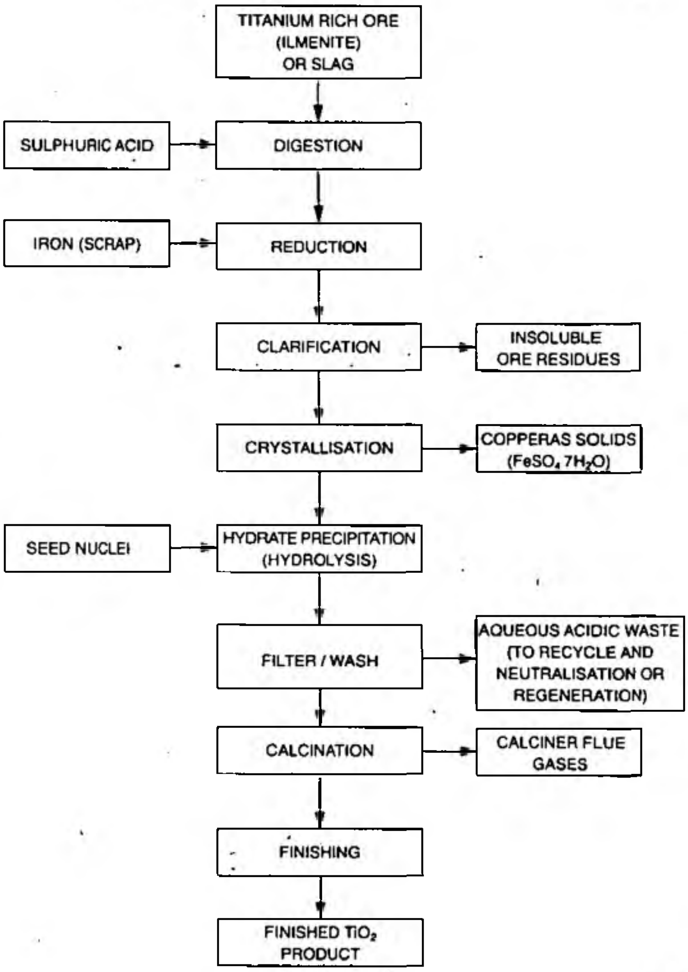
The processes are:

- the chloride process, which is described in Section 2.4.5(f); and
- the sulphate process, which uses sulphuric acid to digest the prepared titanium dioxide ore, and which is described in this section.

The sulphate route uses low-concentration ores such as ilmenite but can also use higher-concentration synthetic slags. The greater presence of impurities, however, leads to more waste from the process. Both crystalline forms of TiO_2 can be readily formed.

The process generally consists of the following sequential stages (see Figure 2.7, for a typical block flow scheme).

Figure 2.7 ***Outline flow diagram (Sulphate process)***



Drying and grinding

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

Digestion

Digestion of the ore can be operated either batchwise or continuously. The more usual process is batch. The ground ore is mixed with concentrated sulphuric acid in a digester. The highly exothermic reaction is initiated by the introduction of a measured quantity of steam and takes place at around 150°C.

The equation for the digestion reaction may be summarized as:

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + 2H_2O + FeSO_4$$

During the batch process the exothermic reaction raises the temperature of the reactor from 180 to 200°C and water is evaporated. Agitation/mixing of the reactor is generally achieved by air blowing. The off-gases also contain sulphur dioxide, which must be scrubbed. A solid 'cake' is formed towards the completion of the reaction. This is subsequently dissolved in cold water.

Extreme care has to be taken to ensure that the reaction does not run away and result in an explosion. The vessel area is evacuated before the steam is introduced.

The primary product from the reaction is titanyl sulphate ($TiOSO_4$) but both ferrous and ferric sulphates are produced as by-products.

Reduction

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

Clarification and crystallisation

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

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

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

Hydrolysis

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

The hydrolysis reaction is:

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

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

Filtration and leaching

The precipitate is washed and dried on vacuum filters to remove trace metal salts. Resultant solid is slurried with dilute sulphuric acid and either zinc or trivalent titanium is usually added as a reducing agent.

The slurry is 'leached' at 50°C to remove final traces of iron and undergoes final washing and drying. Conditioning agents are added at this point to the resulting pulp to enhance crystallite growth.

The filtrate is strongly acidic and either can be reconcentrated and recycled back to the process or may be neutralised with lime/limestone and the product gypsum sold for wallboard manufacture etc.

Calcination

The rotary kilns are directly fired with oil or gas. The pulp moves under gravity counter-currently to the combustion gases. Water and oxides of sulphur are driven off the pulp. Temperature control is important in the production of the correct crystalline form of the pigment.

Solids processing

The resulting solid is cooled, milled, coated, micronised and packed. Two stages of milling are used:

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

The TiO_2 particles are coated with other oxides (eg aluminium/silicon/zirconium) to improve durability and may be coated with organic materials to promote dispersion. These may have an effect on the toxicity of the final product (TiO_2 is classed as a nuisance dust).

Abatement systems for the sulphate process for TiO_2 production

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

- Ferrous sulphate being re-converted to ferric form, which is used in water treatment.
- Spent acid being either regenerated or treated with chalk to produce white gypsum (for wallboards) and red gypsum (agricultural use).
- A high-quality CO_2 may be produced during gypsum manufacture. This may be bottled and sold for carbonated drinks.

Abatement of oxides of sulphur releases resulting from reaction of the ore with sulphuric acid is via the processes described in Section 2.2.1.

Releases to air

- Oxides of sulphur from digester.
- Oxides of sulphur from kilns.
- Oxides of carbon from kilns.
- Particulate matter from kilns, dry milling and materials handling.

Releases to water

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

Releases to land

- Unreacted ore and residue from the digesters.
- Solids from strong acid filtrate neutralisation or the acid process.

(b) Manufacture of alkali-metal and ammonium sulphites

Introduction

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

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

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

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

The SO_2 released by each system will be different depending upon whether the product is formed under alkaline or acid conditions. For integrated plants, to minimise the duty on a final scrubber, it is best that the low-pH product is formed from the strong gas strength while the alkaline product is formed under the leaner gas conditions further down the absorption series.

This permits the exhaust SO_2 from one process to be used in another, thus minimising overall SO_2 emission levels. Typically total sulphur loss should be less than 0.15%.

Manufacture of sodium metabisulphite

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

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

Manufacture of sodium sulphite

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

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

Manufacture of sodium hydrogensulphite

Sodium hydrogensulphite (sodium bisulphite, $NaHSO_3$) more often results from removing SO_2 from the gas before exhaust to atmosphere. It exerts a higher vapour pressure than sodium sulphite. This would principally compel production to be located earlier in the gas absorption sequence of an integrated plant.

Operational advantages exist over the sulphite for using it in abatement since it removes twice as much SO_2 for the same caustic requirement. It is also more soluble, thereby enabling a more concentrated yet solids-free scrubbing system to be used.

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

Manufacture of sodium thiosulphate

Sodium thiosulphate ($Na_2S_2O_3$) is made by oxidising sodium sulphite or hydrogensulphite with excess sulphur. This can therefore use any excess hydrogensulphite and has the added advantage that impure or recovered sulphur, eg sulphur spillages from other processes, can be used.

Hydrogen sulphide gas is released, which requires scrubbing. The product has to be filtered to remove the excess sulphur and impurities. The filter cake is disposed of to land.

Manufacture of potassium sulphites

Potassium sulphite (K_2SO_3) is manufactured in a similar way to sodium sulphite.

Potassium hydrogensulphite ($KHSO_3$) is manufactured in a similar way to sodium metabisulphite.

Manufacture of ammonium hydrogensulphite

Ammonium hydrogensulphite (ammonium bisulphite, ABS, NH_4HSO_3) is manufactured in either single-or-double-stage counter-current absorption plant. The first stage contacts neat burner gas with the liquid product from the second stage at a pH of about 5.5. Ammonia solution is added to the second stage and contacts the gas from the first stage at a higher pH. Control of this pH is important – too low and SO_2 will be lost, too high and ammonia will be stripped out and cause deposition fouling downstream.

Releases to air

- Sulphur dioxide from vents and tail scrubber.
- Hydrogen sulphide from sodium thiosulphate reactor.
- Ammonia from ammonium hydrogensulphite plant.
- Particulate from material handling and dryers.
- Hydrogen sulphide from liquid sulphur storage.

Releases to water

- Spillages from all plant.
- Drainage from bunded storage tanks.

Releases to land

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

Abatement

Abatement technology is generally conventional SO_x scrubbing technology, with the maximum re-use of recovered SO_2. Particulate from the burner and mists are removed from the tail gas by 'Brinks' mist eliminator and electrostatic precipitation. The former also knocks out ammonia and the latter SO_x as weak sulphuric acid. BAT will involve recycle or sale for spent acid recovery (see Section 2.2.6).

2.3 Nitric acid

2.3.1 Manufacture of medium-concentration nitric acid

(a) General

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

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

- catalytic oxidation of ammonia (NH_3) to nitrogen monoxide (NO);
- oxidation of nitrogen monoxide to the dioxide (NO_2); and
- absorption of the nitrogen dioxide in water to produce medium-concentration nitric acid (HNO_3) accompanied by the release of one nitrogen monoxide molecule for every three molecules of NO_2 absorbed.

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

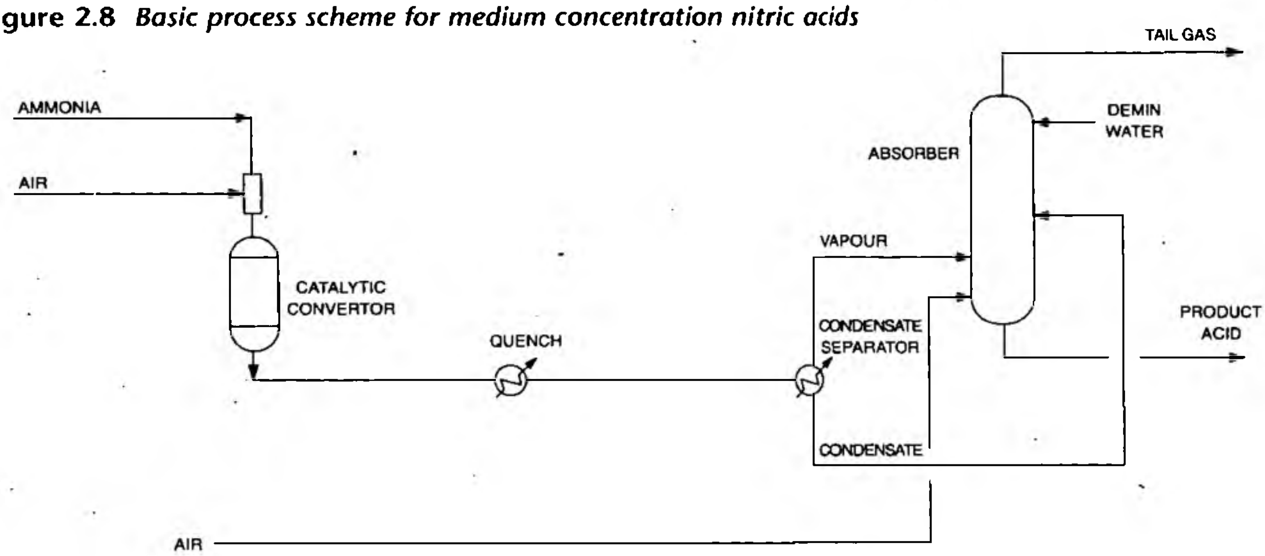
The 'single' pressure system operates the ammonia oxidation step at essentially the same pressure as the absorption section with 'low single pressure' plants operating at a pressure below 1.7 barg, 'medium single pressure' plants operating at 3–6.5 barg and 'high single pressure' plants operating above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

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

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

A nitric acid plant is mainly constructed from stainless steels selected for these specific duties, with nickel alloys, titanium or

Figure 2.8 ***Basic process scheme for medium concentration nitric acids***



zirconium used in some of the more hostile environments. In particular, during the heat recovery process, nitric acid will pass through an acid gas dew-point regime. Cooler tubes may be subject to alternate drying/wetting/evaporation zones. Corrosion is also more of a problem with higher-pressure plants.

A basic process scheme for medium-concentration nitric acid is shown in Figure 2.8.

(b) Ammonia oxidation

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

$$4NH_3 + 5O_2 = 4NO + 6H_2O \qquad (1)$$

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

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \qquad (2)$$

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \qquad (3)$$

All three ammonia oxidation reactions are highly exothermic.

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

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

The selectivity of the reaction and the yield of nitrogen monoxide from the catalytic oxidation of ammonia are dependent on temperature and pressure. The lower the temperature and pressure, the higher the yield. Optimum temperatures for catalytic oxidation to NO are in the range 800–950°C but, whilst reactors designed for operation at 1 barg can achieve yields of NO from NH_2 of 97–98%, modern plant designs tend to favour operation at 'medium' pressure (3–5 barg) where the yield is around 96%.

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

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

(c) Oxidation of nitrogen monoxide

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

$$2NO + O_2 = 2NO_2 \qquad (4)$$

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

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

(d) Reaction of nitrogen dioxide with water

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

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

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \qquad (5)$$

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

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

$$NO_{(g)} + NO_{2(g)} + H_2O_{(l)} \rightleftharpoons 2\ HNO_{2(l)} \qquad (6)$$

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

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

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

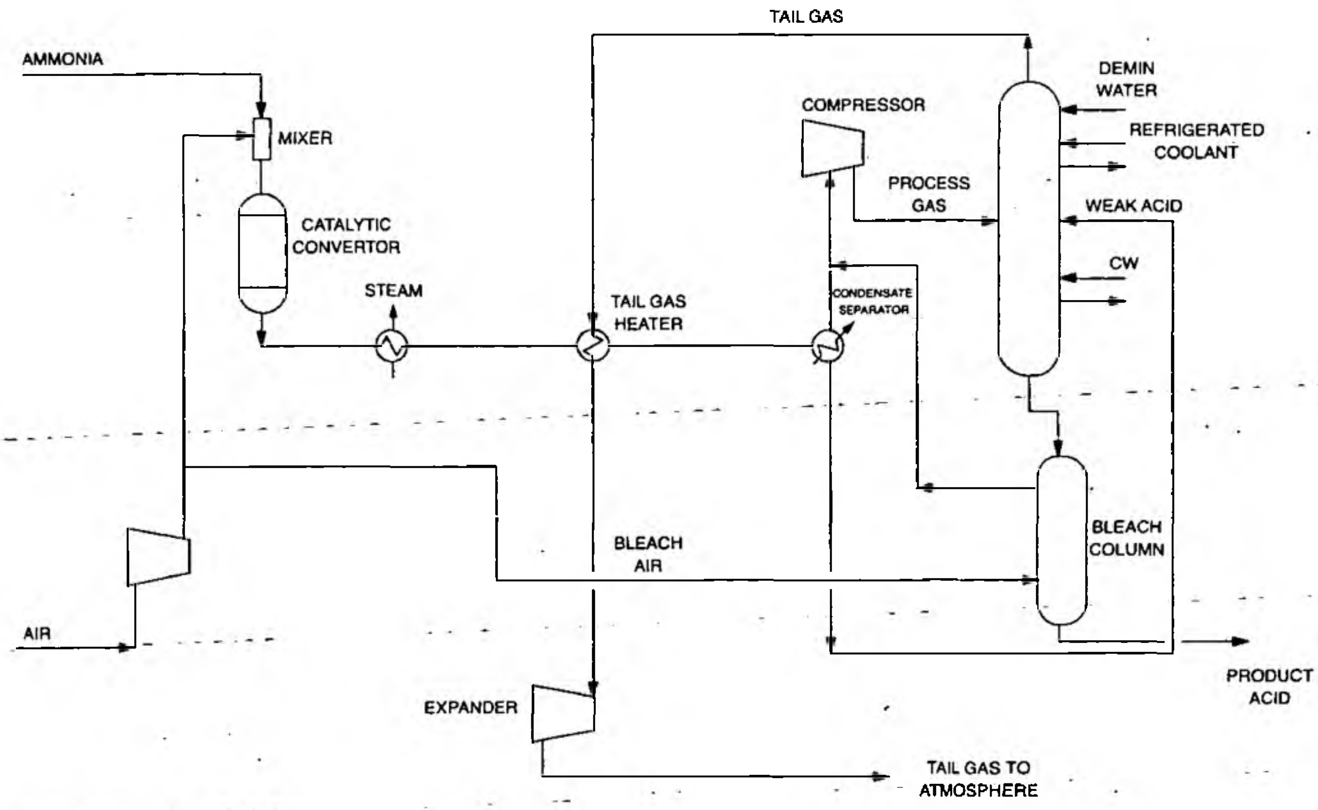
(e) Typical dual pressure plant description

A simplified flow diagram is given in Figure 2.9.

Liquid ammonia from storage is evaporated and superheated to ensure that no liquid carry-over occurs, which can give rise to catalyst gauze damage, loss of ratio control and consequent risk of operation within the explosive range. Filtering is necessary where carbon steel has been used in the construction of the ammonia storage and vaporising vessels, as rust must be removed from the ammonia stream. Certain plants avoid this problem by using stainless steel lines and vessels.

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

Figure 2.9 Simplified dual pressure flow diagram: medium concentration nitric acid



Filtering of the two streams is generally carried out separately to minimise the possibility of a preliminary reaction between the ammonia and the air and to prevent catalyst gauze contamination.

The reactor is designed to give a uniform distribution of the ammonia/air mixture over the catalyst gauze.

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

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

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

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

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

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

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

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

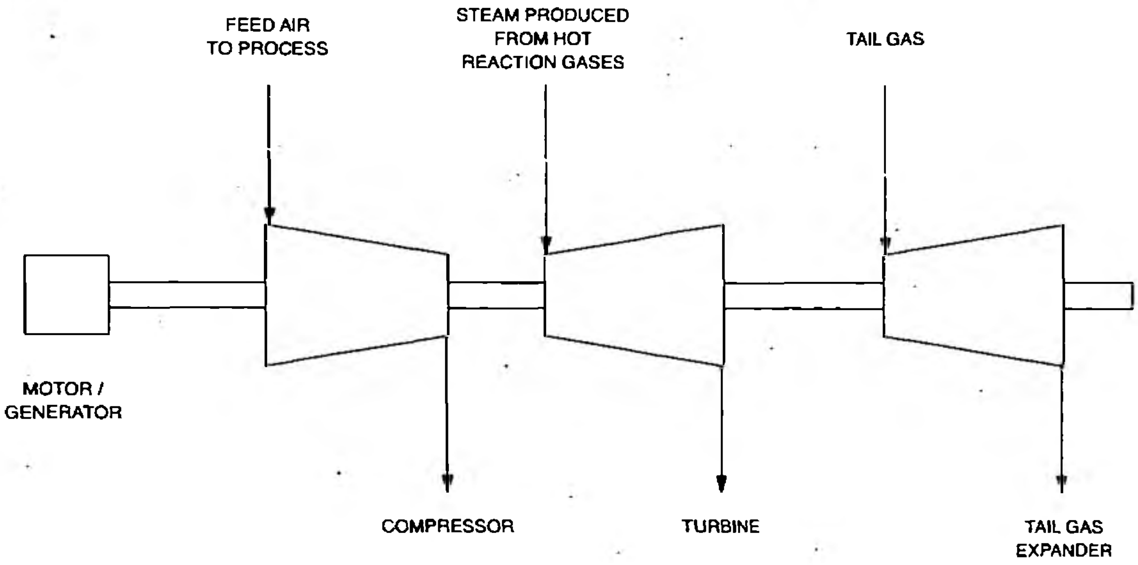
In the 'dual pressure' process the 'nitrous' gas leaving the cooler-condenser is compressed to a higher pressure in preparation for the absorption stage.

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

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

The 'tail gas' from the absorption tower is passed via a turbo-expander and other energy recovery equipment to stack. It should be noted that on nitric acid processes the energy recovery systems are usually highly integrated into the overall design of the plant. Figure 2.10 shows a typical arrangement for a turbo-compressor train with energy recovery. Waste heat boiler steam and the tail gas are used to drive turbines to:

Figure 2.10 ***Simplified diagram of medium concentration nitric acid integrated drive train***



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

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

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

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

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

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

(f) Single pressure plant description

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

(g) Advantages and disadvantages of the dual pressure process

The reactions occurring in the ammonia oxidation catalytic reactor and the absorption tower are both highly dependent on pressure and temperature (see Section 2.3.1 (b) and (d)).

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

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

(h) Potential release routes

Releases to air

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

Releases to water

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

Releases to land

- None.

2.3.2 Manufacture of high-concentration nitric acid (95–100% HNO_3)

(a) Introduction

Because of its low demand, only relatively small-scale processes have been developed for the manufacture of high-concentration nitric acid (96–100 wt %).

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

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

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

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

(b) Extractive distillation using sulphuric acid

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

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

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

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

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

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

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

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

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

(e) Potential release routes using sulphuric acid

Releases to air

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

Releases to water

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

Releases to land

- None.

(d) Extractive distillation using magnesium nitrate

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

(e) Potential release routes using magnesium nitrate

Releases to air

- Oxides of nitrogen from the acid condenser or final absorber.

Releases to water

- Weak nitric acid effluent from plant wash-down.

Releases to land

- None.

(f) Distillation of superazeotropic acid

Figure 2.11 shows a process flow diagram of the direct concentrated nitric acid route.

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

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

The reaction gases, mainly nitrogen monoxide, are cooled to a temperature low enough to condense all the reaction water in the form of weak acid (2% HNO_3).

The dry gases enter the oxidation tower, where, in contact with around 60% nitric acid, the nitrogen monoxide reacts with nitric acid in the reverse of the normal nitric acid absorption reactions to produce nitrogen dioxide:

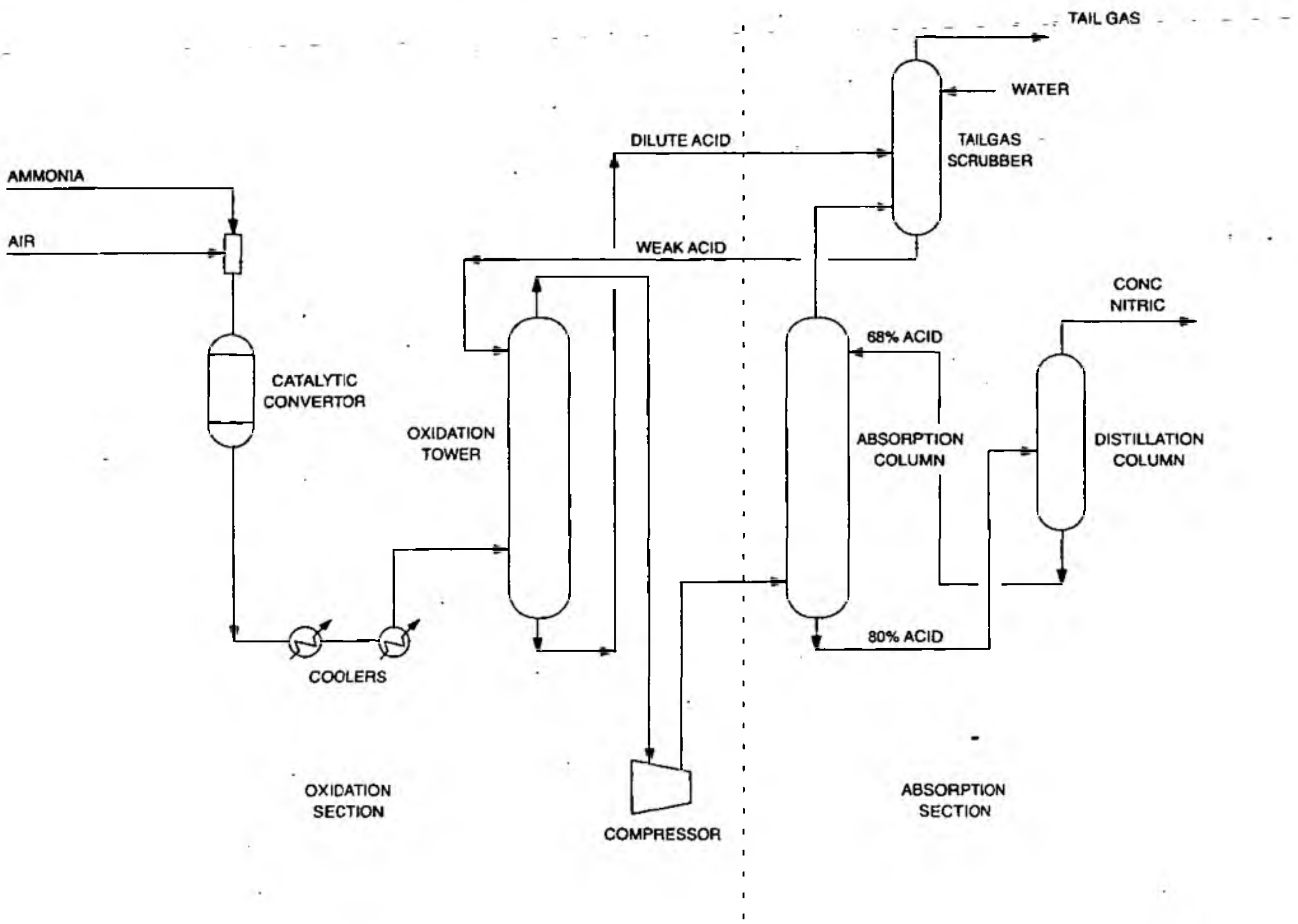
$$NO + 2HNO_3 \rightleftharpoons 3NO_2 + H_2O$$

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

The depleted nitric acid from the oxidation tower is pumped to the weak-acid absorption tower for re-strengthening to 60%.

The enriched NO_2 stream from the oxidation tower is then compressed to about 11 barg, cooled and passed to the strong-acid absorption tower where 68% nitric acid is flowing counter-currently. At this point, the nitrogen dioxide partial pressure in the gas is high enough to produce 80% concentration nitric acid when absorbed in azeotropic nitric acid (68% HNO_3).

Figure 2.11 *Simplified flow diagram: direct route concentrated nitric acid*



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

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

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

(g) Potential release routes from superazeotropic acid

Releases to air

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

Releases to water

○ Weak nitric acid effluent from plant wash-down.

Releases to land

○ None.

2.3.3 Abatement techniques for nitric acid manufacture

(a) General

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

Associated with the nitric acid manufacturing plant will be the ammonia storage and handling systems. Fugitive gaseous ammonia emissions may occur from this equipment, ie from vents and pressure relief devices. The techniques for preventing, or minimising and rendering harmless, releases of ammonia to the environment should include good maintenance and housekeeping practices and leak detection checks. These are covered under a separate IPC Guidance Note, S2 4.04, on inorganic chemcials(8).

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

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

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

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

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

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

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

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

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

(b) Abatement techniques

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

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

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

(c) Scrubbing using sodium hydroxide solution

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

$$NO + NO_2 \rightleftharpoons N_2O_3$$

$$N_2O_3 + 2NaOH \rightarrow 2\ NaNO_2 + H_2O$$

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

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

$$2NO_2 + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O$$

Surplus nitrogen monoxide does not react with the sodium hydroxide.

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

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

Scrubbing techniques have used a range of chemicals including:

- sulphuric acid;
- ammonia; and
- urea.

(d) Extended absorption

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

If extended absorption were to be employed it is most probable

Table 2.1 *Summary of abatement techniques nitric acid plants.*

Control technique	Environmental impacts				Typical NO_x (mg/m³)	Salient features	Applicability
	Air	Liquid	Solid	Energy			
Molecular sieve	None.	None.	None.	Extra fuel for regeneration.	20	High capital. Cyclic operation. adsorption	No recent examples of use of process. Good turndown. Can be added easily to existing plant.
Extended Absorption	None.	None.		Pumps and refriguration.	205–410	High capital if retrofitted; modest capital as integral part of plant design. Limited suitability on LP processes.	Industry standard for new plants.
NSCR	Possible CO. Increased CO_2 emissions.	None.	Catalyst disposal.	Increased fuel consumption. Potential for energy recovery.	205	High capital multiple beds with intercooling for low emissions. Removes N_2O.	Tending to be superseded by SCR.
SCR	Ammonia slip.	None.	Catalyst disposal.	Small quantity of ammonia required.	100	Does not remove N_2O.	Can be added to existing plants.

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

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

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

Other options for extended absorption are:

1. High-pressure absorption at up to 17 bar. To run the whole back end of the plant at pressure will usually require the use of exotic materials of construction. It is claimed that the use of titanium and zirconium can result in cost-effective design.

2. Oxygen injection. Two advantages accrue from the use of increased oxygen as opposed to air in the feed to the bleach column. First, the mass of the tail gas stream is reduced, which reduces the total emission to atmosphere. Secondly, an increase in the partial pressure of oxygen in the system increases the concentration of oxygen in the liquid film. The absorption of NO_x in water to give nitric acid is the sum of two reactions:

$$H_2O + NO + NO_2 \rightleftharpoons 2HNO_2$$

$$3HNO_2 \rightarrow 2NO + H_2O + HNO_3$$

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

$$2HNO_2 + O_2 \longrightarrow 2HNO_3$$

with a corresponding decrease in NO_x emissions in the tail gas.

Molecular sieve adsorption

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

(e) Non-selective catalytic reduction

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

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

Process description

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

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

- Hydrogen – 200°C minimum, typically 300°C.
- Naphtha, LPG – 350°C minimum, typically 450°C.
- Natural gas – 480°C minimum, typically 550°C

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

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

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

The reactions with different fuels are given below:

- *Reduction of oxygen*

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$2H_2 + O_2 \rightarrow 2H_2O$$

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

- *Reduction of nitrogen dioxide*

$$CH_4 + 4NO_2 \rightarrow CO_2 + 2H_2O + 4NO$$

$$H_2 + NO_2 \rightarrow H_2O + NO$$

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

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

- *Reduction of nitrogen monoxide*

$$CH_4 + 4NO \rightarrow CO_2 + 2H_2O + 2N_2$$

$$2H_2 + 2NO \rightarrow 2H_2O + N_2$$

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

- *Reduction of Nitrous oxide*

$$CH_4 + 4N_2O \rightarrow CO_2 + 2H_2O + 4N_2$$

$$H_2 + N_2O \rightarrow H_2O + N_2$$

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

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

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

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

- Hydrogen 160°C
- Methane, naphtha, butane,propane 130°C

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

Two stages of catalytic treatment are generally only required when methane is the fuel because methane requires the highest catalytic operating temperature. Even so, when two stages are used an intercooler is not usually necessary. It is avoided by admitting the total fuel requirement before the first stage, thereby inducing reforming of the excess methane to carbon monoxide and hydrogen, which is an endothermic reaction.

However, it is now common practice to reduce the oxygen levels in the tail gas to a minimum, by carefully controlling the airflow in the bleaching tower, such that only one pass is required over the catalyst.

The hot gas leaving the system, at a temperature up to 750°C, can be used to generate steam and/or power via a gas turbine (see Figure 2.10). One disadvantage of extensive integration, particularly with hydrogen-based NSCR, is that loss of hydrogen results in immediate loss of abatement. The nitric acid plant therefore needs to be shut down until hydrogen is restored.

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

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

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

NSCR catalysts are long-lived and need replacement every two to three years.

The disadvantages of using a hydrocarbon as opposed to hydrogen as the reducing agent is that the treated tail gas can contain quantities of carbon monoxide (up to 1250 mg/m³) as well as unreacted and partially converted hydrocarbon.

(f) Selective catalytic NO_x-reduction with ammonia

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

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

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

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6\,H_2O$$

$$NO + NO_2 + 2\,NH_3 \rightarrow 2\,N_2 + 3\,H_2O$$

$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O$$

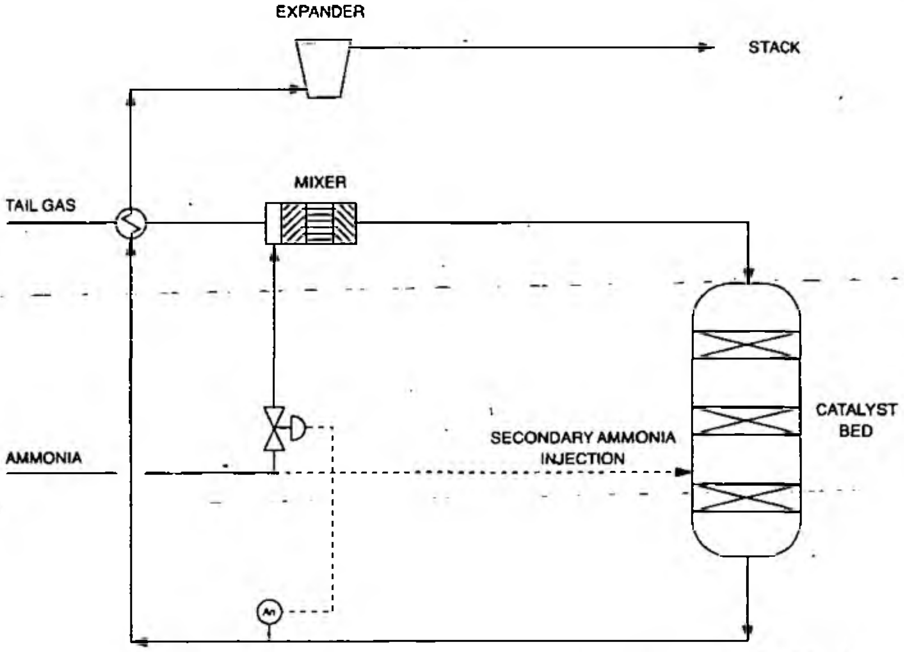
There are also small quantities of ammonium nitrate and nitrite formed by the reaction of the ammonia and nitrogen oxides. Catalysts commonly used are vanadium pentoxide, platinum, iron/chromium oxide mixtures or zeolites.

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

Process description

An outline of the SCR flowsheet is given as Figure 2.12.

Figure 2.12 ***Outline of SCR flowsheet***



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

The efficiency of the conversion of the NO_x gases can be in excess of 95%. Theoretically no excess ammonia is required, but in practice, due to ammonia slippage through the catalyst, some excess ammonia may be required and thus may give a release level of up to 10 mg/m³ from the plant stack.

The ammonia addition can be controlled to match a varying inlet NO_x concentration to ensure that the required outlet concentration of NO_x can be consistently achieved.
It is evident that the use of this abatement process involves increased ammonia consumption. However, for plants with small capacities (say, less than 100 tonnes/day of acid), with medium-pressure absorption and a NO_x content of 1200 mg/m³, as NO_2, in the tail gas, the process can be economically attractive compared to a high-pressure absorption plant designed to achieve the same low release limit for NO_x.

(g) Comparison of nitric acid plant abatement systems

Conditions selected by the operator should be demonstrated to be the best practicable for optimum abatement of NO_x. Both catalytic reduction techniques and extended absorption are capable of achieving 200 mg/m³ NO_x for new plant.

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

For retrofitting of abatement equipment to existing nitric acid plants where the tail-gas NO_x concentration is in the range 600–3000 mg/m³, as NO_2, caustic absorption is unlikely to be a satisfactory option, even when beneficial use can be made of the sodium nitrite/nitrate produced. There is also an associated operational problem since sodium nitrate has a tendency to freeze during the winter months.

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

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

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

The disadvantages of SCR with ammonia are:

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

The advantages of NSCR relative to SCR are:

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

The disadvantages of NSCR relative to SCR are:

- unless hydrogen is used the tail-gas from the absorber has to be preheated to a higher temperature;
- the abatement system can only be started-up after the ammonia oxidation and NO_x absorption sections have stabilised and oxygen in the gas passing to the NSCR

section is less than 3% – otherwise the temperature rise across the catalyst will be too high;

- unless hydrogen is used, significant concentrations of carbon monoxide (up to 1250 mg/m³) and hydrocarbons are released in the tail-gas.;
- hydrogen, if provided from a refinery unit, is less reliable and may result in more frequent shut-downs; and
- the system is not available as an add-on system because of the need for a high-temperature gas expander.

(h) Start- up and transient plant conditions

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

It can take up to an hour to establish stable operating conditions after process air compressor start-up although not at rated capacity, which may take several hours.

Ammonia oxidation

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

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

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

Catalytic abatement systems

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

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

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

Nitric acid systems often have highly integrated energy systems as mentioned previously and shown in Figure 2.10. This would make the retrofitting of units with NSCR difficult. Not only would it require a change to the energy balance across the whole unit, but often the compressors, expanders and motors are located on one drive shaft in a 'train' configuration such that any changes would mean reconfiguring the train.

2.3.4 Best available techniques

New large nitric acid plants can be designed to operate under steady conditions with a tail - gas concentration of less than 200 mg/m³, as NO_2, utilising extended absorption at high pressure with refrigeration followed by SCR treatment of the tail gas. Alternatively best available techniques (BAT) may be achievable by absorption down to these levels, which would require optimal tower design, operation at a pressure of around 11 barg or above and top tower temperatures below 15°C.

Depending on the comparative environmental impact of N_2O and NO_x, the use of NSCR may be justified. BAT for existing plant would include retrofitting plants that do not include tail gas abatement with a suitable system such that emissions are reduced to less than 300 mg/m³. The use of caustic scrubbinbg to produce co product sodium nitrite may also be BAT and can achieve a level of 200 mg/m³.

During start-up conditions transient releases up to 1000 mg/m³ may be experienced.

2.3.5 Processes giving rise to the release of oxides of nitrogen

Relevant inorganic chemical processes are classified as follows:

- metal brightening ;
- metal pickling; and
- dissolution of metals and metal alloys.

Metal brightening and metal pickling are now covered under Part A only when they form part of another Part A process.

Metal brightening- the anodising of *aluminium*

Metal brightening techniques can be applied to non-ferrous metals and their alloys to improve appearance. The bright anodising of aluminium is such an application, which is explained briefly below.

Anodising refers generally to the process used for creating a decorative and protective surface finish to aluminium and its alloys.

Nitric acid is commonly used in the pre-treatment and post-treatment processes applied to components undergoing anodising and can give rise to the release of oxides of nitrogen.

The specific anodising operation involves the promotion of a passive aluminium oxide surface layer on aluminium components by electrochemical action.

The basic steps involved in the overall anodising process are:

- cleaning and degreasing;
- surface brightening;
- anodising; and
- dyeing and sealing.

Additionally, intermediate washing operations (rinses) take place between the main process steps above, including "de-smutting" to remove surface contamination.

Cleaning and degreasing

The removal of oil, grease, polishing composition, dirt, etc, is most commonly achieved using alkaline solutions, although acid or solvent cleaners can be used.

Surface brightening

This process step serves to smooth (level) any surface irregularities and provides a bright reflective finish prior to anodising. Surface brightening can be achieved in two ways:

- Electro-brightening involves passing a DC current through an electrolyte bath with the workpiece forming the anode. This process does not give rise to NO_x emissions;

- Chemical brightening uses a mixed acid solution containing principally phosphoric acid, nitric acid and sulphuric acid with other additions including wetting agents and anti-fuming agents. It is this process step that principally gives rise to emissions in the form of NO_x which must be mechanically extracted and treated before discharge to atmosphere.

The greatest release occurs when the workpiece is being removed from the bath but lesser continuous releases do occur from the surface of the bath in normal operation at a temperature of 100–110°C.

Anodising

A protective oxide layer is developed on the aluminium by passing a low-voltage DC current through an electrolyte bath with the immersed workpiece acting as the anode. The electrolyte can be alkaline but most commonly sulphuric acid is used with a typical strength range of 15-25 wt%. Phosphoric and chromic acids can be used for special applications.

To achieve a satisfactory finish the anodising bath must be agitated either by air sparging or by external recirculation possibly including electrolyte cooling. A concentration of aluminium builds up in the electrolyte during anodising and must be controlled by partial dumping of the bath contents or by continuous purging, usually to an effluent treatment plant.

A technique known as 'hard anodising' is achieved using chilled electrolyte to produce a denser surface oxide layer.

Dyeing and sealing

The aluminium workpiece can be dipped in organic or inorganic dyes to produce coloured finishes; electrolytic colouring techniques are also available. Inorganic pigments containing heavy metals may find use in dyeing operations.

To maintain the colour finish attained by dyeing, the surface must be sealed. This can be achieved by:

- physical sealing using a protective coating such as a solvent- based substrate;

- water sealing using boiling de-ionised water;

- chemical sealing of the oxide surface by reaction with a chemical solution; and

- chemical sealing using nickel acetate and cobalt acetate salts

- de-ionised water is usually required to avoid surface contamination from dissolved salts found in town's water.

De-smut treatments between the key process steps are used to remove surface contamination and these can involve the use of nitric acid, but other reagents are now more common, such as ferric sulphate.

Hydrogen evolved in the anodising tank can carry out some sulphuric acid mist which may require alkaline scrubbing in exceptional cases.

Surface bleaching with nitric acid is sometimes practised to remove old dye from reworked production and may consequently give rise to fume.

The workpiece is immersed in rinse water tanks between the various processing stages; the acid and alkaline waste rinse waters produced, together with other waste streams (ie purge from anodising bath), are usually neutralised in an effluent treatment plant.

(b) Potential release routes from metal brightening

Releases to air

- Oxides of nitrogen from the chemical brightening bath.

Releases to water

- Metallic salts from neutralised waste water.

Releases to land

- Precipitated metal salts following waste-water treatment and dewatering.

(c) Abatement techniques for metal brightening

In non-ferrous metal brightening processes (eg anodising of aluminium) the brightening baths can utilise proprietary mixed acid solutions containing a fume suppressant, which serves to reduce NO_x emissions but will not obviate the need for subsequent abatement before release to air.

A wet scrubbing system may be installed using, most commonly, sodium hydroxide solution (approx. 2 wt%) but in some applications achieving the release limit for NO_x might be difficult.

A wet scrubbing system employing hydrogen peroxide as an oxidising agent will give significantly better NO_x removal efficiency than sodium hydroxide as well as a smaller scrubbing plant albeit at the expense of increased operating cost.

Waste-water streams are usually collected in an effluent treatment plant for neutralisation and solids separation; clarified water may be recycled to process with the solids disposed of to a licensed waste disposal facility.

Consideration should be given to ion-exchange methods, which would allow recycling of spent acid from the anodising process and also for the recovery of metals used in the sealing process.

(d) Metal pickling – stainless steel

Nitric acid is used in the pickling of stainless steels and titanium. The pickling of titanium is not widely practised and the following description concentrates on stainless steel.

The pickling of stainless steel is necessary to remove the metal oxide scale, either by dissolving or by detaching, that has been formed on the surface of the steel during hot working and annealing processes.

Stainless steel pickling is predominantly carried out in a mixture of nitric acid and hydrofluoric acid. The concentrations of the two acids used varies according to the quality of the stainless steel to be pickled.

For austenitic stainless steels (16–26% chromium, 6–22% nickel, 0.15% carbon), typically a solution containing 15% –17% nitric acid and 2%–2.5% hydrofluoric acid is used.

For ferritic stainless steels (12–18% chromium, up to 1% nickel, 0.1% carbon), typically a solution containing 10% nitric acid and 1% hydrofluoric acid is used.

Process description

Pickling can be done as a batch, semi-batch, or continuous process and can also involve a number of stages using different baths.

All forms of stainless steel (ie sheet, plate or tube) can be pickled, but the following process description considers a continuous line operating with the steel in the form of a coil. This coil is sometimes referred to as a 'black hot band coil', the 'black' term referring to the colour of the scale deposit. Each of the steps described in the continuous line can be carried out as an individual batch process.

Before passing into the acid baths the steel is first annealed and may then require shot blasting. The shot blasting process is carefully controlled so as to remove most of the scale but not damage the steel.

The operations carried out on the pickling lines take place either in totally enclosed equipment or in equipment fitted with hoods. In either case the units are under continuous extraction. The modern design of bath recirculates the acid using an external pump through nozzles mounted within the bath creating agitation and improving reaction conditions.

Sludge formation increases rapidly once there is more than approximately 5% iron in the acid solution.

The pickling process is carried out at temperatures up to 70°C dependent upon the steel quality.

The reaction between austenitic stainless steel and the acid solution is slightly endothermic and heat can be added to the baths to control the temperature.

The reaction between ferritic stainless steel and the acid solution is exothermic and cooling of the baths is necessary to control the temperature.

A new development in stainless steel pickling is the dosing of the acid solution with hydrogen peroxide. This reduces the nitrogen oxides emissions and the quantity of nitric acid used.

Pickling chemistry

The chemical reactions taking place during pickling are complex and the following is only a simplistic representation.

The dominating chemical reaction during pickling is the dissolution of metals (Fe, Cr, Ni and Mo) by the nitric acid which then react with the hydrofluoric acid leading to the formation of metal complexes. The following are the reactions for iron (the dominant metal) with nitric acid:

$$Fe + 4H^+ + NO_3^- \rightarrow Fe^{3+} + NO + 2H_2O$$

$$Fe + 6H^+ + 3NO_3^- \rightarrow Fe^{3+} + 3NO_2 + 3H_2O$$

When ferritic stainless steel is pickled the surface is oxidised to create a passive layer.

In the metal dissolution reactions NO_x gases are formed, typically consisting of equal quantities of NO and NO_2.

Some of the liberated NO_x gas reacts with the water present to form nitrous acid in accordance with the following chemical equation:

$NO + NO_2 + H_2O \rightarrow 2HNO_2$

The system of dosing with hydrogen peroxide is based upon the reaction between the NO_x gas and hydrogen peroxide, which forms nitric and nitrous acids, and the reaction between the nitrous acid and hydrogen peroxide to form more nitric acid, all in accordance with the following chemical equations:

$NO + H_2O_2 \rightarrow NO_2 + H_2O$

$NO_2 + NO_2 \rightarrow N_2O_4$

$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$

$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O$

The chemical reaction between nitrous acid and hydrogen peroxide is extremely rapid, much more so than the catalytic decomposition of hydrogen peroxide to oxygen and water, although this reaction does increase with temperature.

Hydrogen peroxide treatment of the pickling acid normally gives a 20–25% saving in nitric acid consumption.

(e) Potential release routes from metal pickling

Releases to air

- Gaseous emissions of the oxides of nitrogen and hydrogen fluoride from the pickling baths.
- Acid mist emissions from the pickling baths.
- Particulate emissions of the metal oxides scale and shot fragments (iron) generated from the shot blasting of the stainless steel.
- Gaseous emissions from acid storage facilities.

Releases to water

- Neutralised acid waste from the effluent treatment plant.
- Fugitive releases of acid solution containing dissolved metal salts from the process.
- Fugitive releases of metal-rich sludge from the pickling baths.
- Fugitive releases of acids from the storage facilities particularly during road tanker transfer operations.

Releases to land

- Metal hydroxide and fluoride waste from the effluent treatment plant.
- Collected dust from the shot blasting (metal oxides and iron).

(f) Abatement systems for metal pickling

Dust abatement technique

Shot-blasting equipment is normally operated with mechanical air extraction. The dust-laden air is passed through a bag filter prior to discharge to atmosphere via a vent stack.

NO_x abatement techniques

The oxides of nitrogen released from the process can be minimised by close control of acid concentrations and temperatures. Pickling baths should be well covered and provided with mechanical fume extraction.

Addition of hydrogen peroxide to the bath can reduce NO_x emissions by oxidising the nitrogen monoxide formed to nitrogen dioxide which is re-absorbed within the bath acid. Emissions of NO_x from the bath can be reduced by up to 70%, although the economics of this technique will need to be assessed in relation to the specific application.

Constant addition of hydrogen peroxide to the bath at a pre-determined rate is commonly used to control the emissions of nitrogen oxides. Improved dosing control may be achieved by measuring the redox potential of the $HNO_3/HNO_2/H_2O_2$ mixture.

Nitrogen oxides released from the pickling baths should be further treated by passing them through a series of packed wet scrubbers.

Where hydrogen peroxide is not used as an oxidant in the pickling baths it can be used as the irrigant in the wet scrubbing system for improved performance, but this may be less efficient than direct injection into the bath.

Scrubbing with sodium hydroxide solution alone is unlikely to achieve the NO_x BAT level unless equipment design allows for the long NO oxidation times required. Caustic solutions will permit recirculation of the scrubbing liquor and will consequently reduce the treated water requirement (which would otherwise be required with water alone) and subsequent waste disposal volume. The presence of nitrates may require effluent treatment before final disposal.

Spent acid disposal techniques

An ion exchange process can be used to achieve recovery and recycling of acid. Dissolved metals and sludge that remain after acid recovery can be treated using conventional effluent treatment techniques involving neutralisation, sedimentation and filtration.

Filtrate should be recycled for process use where practicable. Filter cake containing metal hydroxides is typically disposed of to licensed landfill.

(g) Dissolution of metals and metal alloys - basic principles

Introduction

Almost all nitrates are soluble, so reactions of many metals with nitric acid are used as a route for the manufacture of a wide range of chemicals.

Recycled materials are dissolved in nitric acid to recover precious metals, particularly in the electronics industry.

Process description

It is not possible to cover the specific industry applications in this Note but rather to cover basic common principles. It should be noted that many metal dissolution processes may be more aptly described under Section 4.5 of the Regulations.

The processing steps are usually fairly simple, normally involving batch dissolver vessels to which the metallic material and nitric acid of varying strength are added.

The metal can be in various forms including billets, sheet, wire or small particles. The size and resulting surface area presented affects the rate of dissolution and consequently the rate of evolution of NO_x and other gases. The rate of reaction also depends on temperature and, as reactions are exothermic, it is often necessary to have a dedicated cooling system associated with the reaction vessel. The nitric acid strength, as well as influencing the reaction rate will also give rise to variable proportions of nitrogen monoxide and nitrogen dioxide, which will require treatment.

Gases evolving from the dissolver vessels are mechanically extracted and passed through a scrubbing system before release to atmosphere via a vent stack.

Dependent upon the process application, the solution remaining on completion of the reaction will be either concentrated for subsequent use or neutralised to separate the desired components. The spent liquor remaining after separation may require further treatment for disposal if recycling of wastes is not possible.

Chemistry

In general, the noble metals are not attacked by nitric acid. Tin, arsenic, antimony, tungsten and molybdenum are converted to oxides, while the remaining metals form nitrates. Iron and chromium become passive in concentrated nitric acid, and lead nitrate forms a protective film on lead.

During reaction, part of the nitric acid is reduced to NO_2, NO and N_2O together with nitrogen, hydroxylamine and ammonia, depending upon the temperature of reaction, the acid concentration and the metal involved.

It has been suggested that the primary reaction in all cases is the production of nascent hydrogen, and this is followed by secondary and tertiary reactions. Taking copper in dilute nitric acid as an example, this may be presented in a simplified form as follows:

○ Primary reaction

$$3Cu + 6HNO_3 \rightarrow 3Cu(NO_3)_2 + 6H$$

○ Secondary reaction

$$6H + 3HNO_3 \rightarrow 3HNO_2 + 3H_2O$$

○ Tertiary reaction

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

For comparison the overall reaction of zinc with dilute nitric acid may be presented as follows:

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + 5H_2O + N_2O$$

The mechanisms of formation of NO_x gases arising from the dissolution of metals can be complex but the less obvious side-reactions that occur do not usually affect, to any degree, the basic gaseous oxide constituents that require to be abated.

(h) Abatement techniques for dissolution of metals

Where batch dissolver vessels are used close process control should be exercised to minimise surges in NO_x emissions. This may include:

- ○ adequate temperature controls;
- ○ liquid level indication; and
- ○ size grading of metals used and means to control the feed rate.

Vessels should be adequately enclosed against excessive air ingress and subject to mechanical fume extraction. All emissions should be passed through a scrubbing system before discharge to atmosphere.

Wet scrubbing systems based on packed towers or high efficiency venturi may be employed. The use of reagents such as hydrogen peroxide in the circulating solution will, most likely, be necessary to achieve the required NO_x emission limits.

In a similar manner to that described for the pickling of stainless steel, it may be possible to inject hydrogen peroxide into acid solutions to suppress NO_x emissions. This will only be possible in applications that do not promote unstable decomposition of the oxidant.

2.3.6 Recovery of nitric acid

It may be economic to recover spent nitric acid or the oxides of nitrogen generated in a number of process applications utilising nitric acid. Consequently, it is probable that such practices will be ancillary to other processes that may be more aptly described in other sections of the Regulations(1).

Some examples of nitric acid recovery processes are given below.

(a) Ion exchange in the recovery of spent metal pickling acid

During the pickling of stainless steel, the quality of acid in the bath deteriorates as a result of the process reaction and associated sludge formation.

Spent acids containing dissolved metals are periodically discharged from the process, typically into a settling tank, and then filtered to remove solids prior to feeding to an acid regeneration unit.

In the acid regeneration unit the spent acid is passed through a specially prepared resin bed. The free acid is 'absorbed' into the resin bed whilst the dissolved metals pass through.

The absorber is then regenerated by passing water through the resin to displace the 'absorbed' acids, which are then sent to storage for re-use.

The metal-rich waste stream from the acid regeneration unit is passed to an effluent treatment plant where it is mixed with the rinse waters used to clean the pickling baths.

The combined waste stream is then neutralised, typically using calcium hydroxide, before passing to clarifiers where, with the aid of flocculants, the metal hydroxide precipitates are removed as a sludge.

This sludge is then passed through a filter press or a rotary vacuum filter, and the resulting filter cake is sent to a licensed landfill. The filtrate is returned to the effluent plant settling tank.

Depending upon the process workload, acid regeneration units can save up to approximately 35% of acid by recycling.

(b) Extractive distillation of nitric acid

Although the nitration of organics is covered by a separate IPC Guidance Note S2 4.02(21), such processes may incorporate an acid recovery system as a means to reduce operating costs and which in turn serves to reduce potential waste streams. As an example, the manufacture of nitroglycerine involves an organic nitration using a mixed nitric acid and sulphuric acid solution. The sulphuric acid can be recovered for sale by using steam to drive off the nitric acid preferentially. The nitric acid fume can be condensed for recycle back to the process. This process is similar to that described earlier for nitric acid concentration by extractive distillation.

(c) Absorption of oxides of nitrogen

Other processes using nitric acid give rise to the generation of oxides of nitrogen and the absorption of such emissions in water or weak acid at low pressure may allow recycling of the nitric acid recovered. However, it is unlikely that achievable release levels will be met without further scrubbing of the effluent gases before discharge to atmosphere.

(d) Potential release routes

Releases to air

- Oxides of nitrogen from condenser purge gas scrubber in extractive distillation, or from tail gas scrubbing in low-pressure water/weak acid absorption.

Releases to water

- Weak acid effluent from purge scrubber and from plant wash-down.

Releases to land

- Metal hydroxides and fluoride-containing compounds in filter cake arising from nitric acid recovery using ion exchange methods.

2.4 Halogens

2.4.1 Manufacture of Fluorine

(a) General

Fluorine can be produced by the electrolysis of anhydrous hydrogen fluoride, dissolved in potassium bifluoride. The mixture has a melting point of approximately 80°C and the electrolytic cells are operated in the 85°–90°C temperature range. Operation at these conditions is optimum and processing advantages include:

- low HF vapour pressure;
- use of tempered water as coolant;
- less corrosion at the anode; and
- accommodation of wider variations in electrolyte composition.

The principal reactions are:

$$2HF \rightarrow F_2 + H_2$$

$$2KHF_2 \rightarrow 2KF + F_2 + H_2$$

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

Fluorine is produced under a slight positive pressure (50 mm water gauge). Nitrogen, introduced via sealing glands, serves both as a padding medium and as a carrier gas. The gas mixture is often fed directly to the user process.

In circumstances involving the bottling of the nitrogen/fluorine mixture, the gas is fed direct from dedicated cells to a compressor. No inventory of pure gaseous fluorine is maintained.

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

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

(b) Potential release routes

Releases to air

- Fluorine, hydrogen fluoride and hydrogen from absorbers.

Releases to water

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

Releases to land

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

2.4.2 Manufacture of chlorine

(a) General

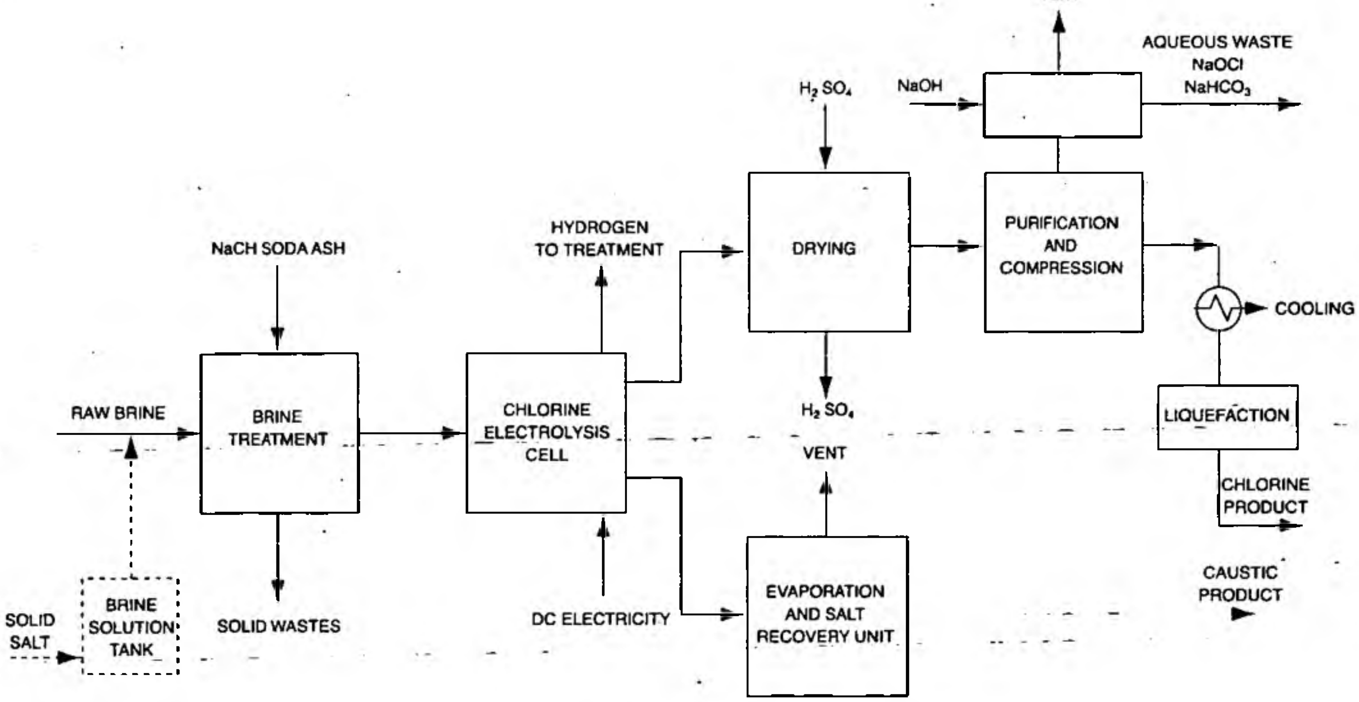
Chlorine is mainly produced by the electrolysis of sodium chloride brine or occasionally potassium chloride brine. It is also manufactured as a by-product in the electrolysis of fused salts or fused mixed salts, eg sodium chloride/calcium chloride/barium chloride producing sodium metal, or sodium chloride/calcium chloride/magnesium chloride producing magnesium, or lithium chloride/potassium chloride producing lithium. The basic process for the electrolysis of brine is shown in Figure 2.13.

(b) Purification of brine

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

Feed brine may also be produced in a resaturation process where imported pure salt or rock salt is added in controlled quantities to a recycled mother liquor. Purification by pH adjustment, precipitation, flocculation and filtration is required,

Figure 2.13 *Chlorine production process*



on a full flow or side stream basis, to keep levels of impurities at the required concentration. Membrane and mercury cells may use recycled brine requiring dechlorination by acidification, vacuum stripping and air blowing.

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

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

(c) Electrolysis of brine

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

The overall reaction involved is:

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$$

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

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

Diaphragm cell

Figure 2.14 provides an illustration of the basic cell. The anode area is physically separated from the cathode area by a permeable asbestos-based diaphragm. Saturated brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment.

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

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

The special waste problem of the diaphragm process arises from the use of asbestos for the diaphragm. Asbestos waste is subject to the Asbestos Regulations and requires specialised handling and landfill requirements.(22)

Mercury cell

An arrangement for the mercury cell is given in Figure 2.15. In this process, mercury flows down the inclined base of the cell, forming the cathode. The hot saturated brine flows co-

Figure 2.14 ***Simplified diaphram cell***

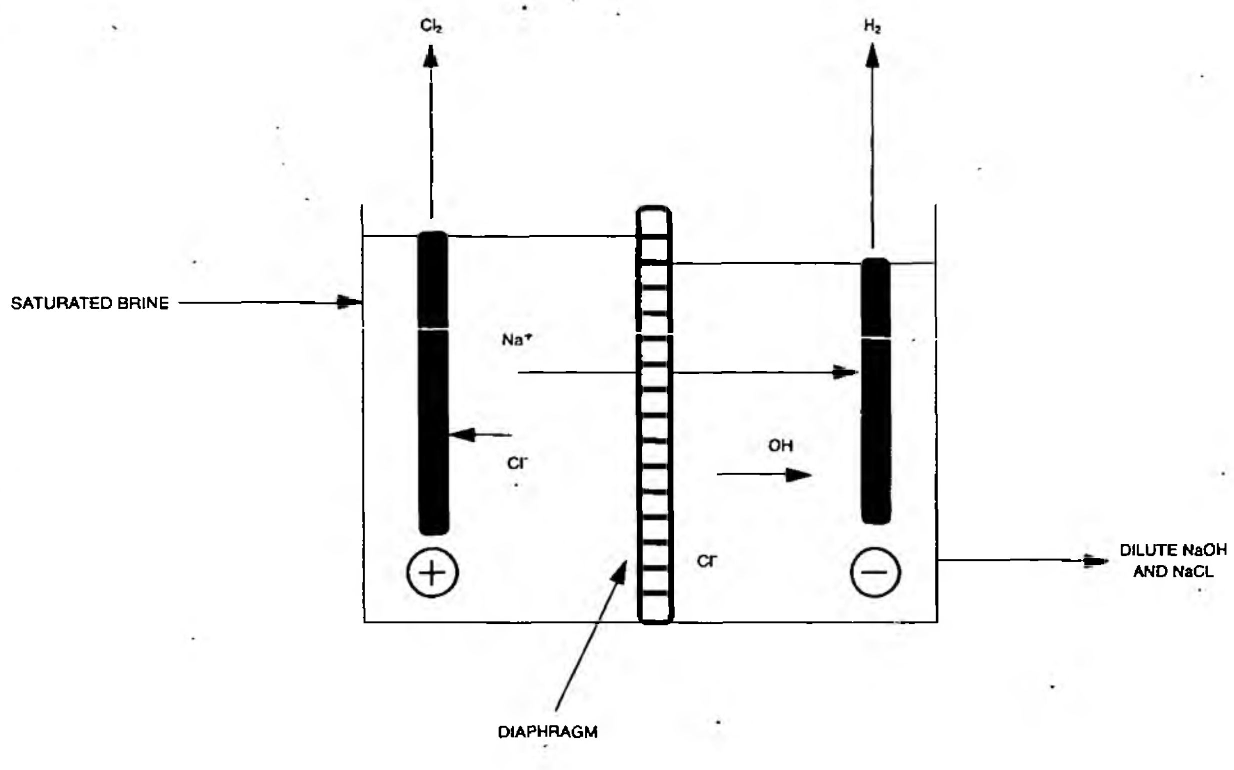
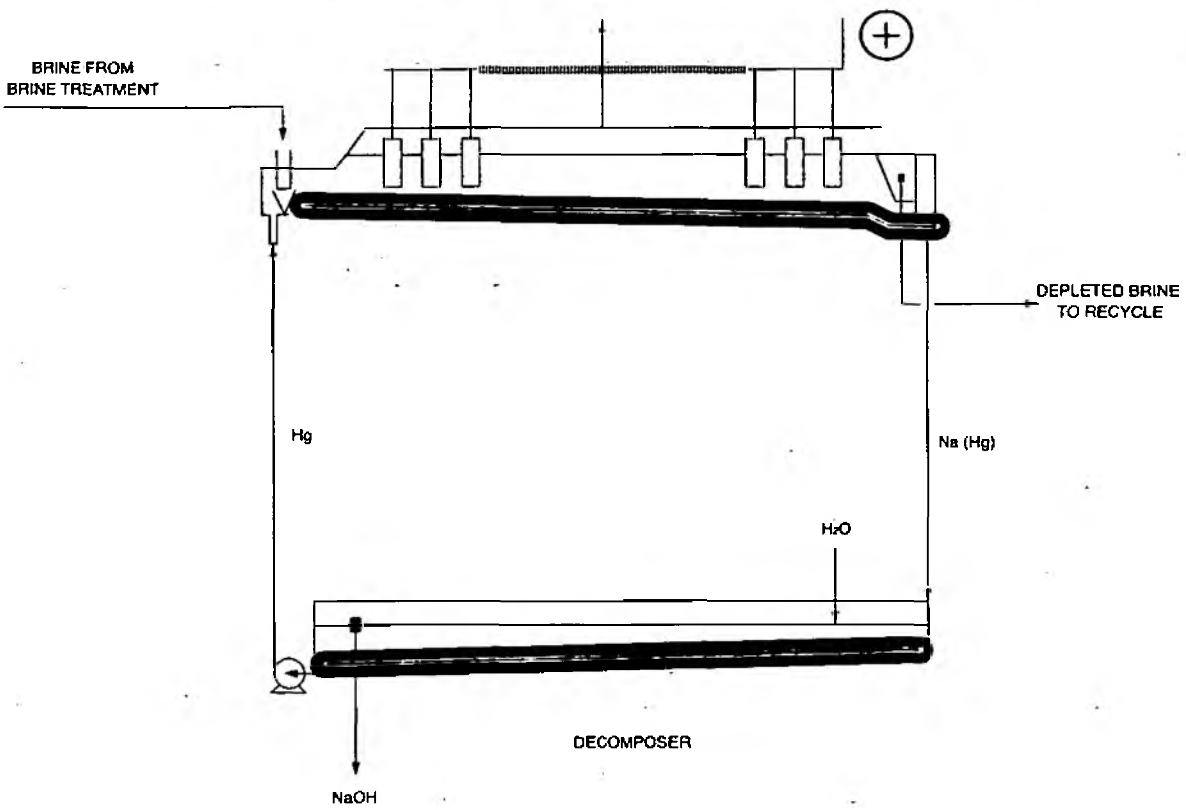


Figure 2.15 ***Mercury cell***



currently on top of the mercury and anodes are suspended in the flowing brine. Mercury cell technology is well established but, due to environmental concerns relating primarily to releases of mercury, intergovernmental pressure favours replacement of the mercury cell by other cell types.

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

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

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

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

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

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

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

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

Membrane cell

A typical membrane cell is shown in Figure 2.16. Membrane cells are assembled on the same principle as filter presses/plate heat exchangers in layers of membranes separated by spacers. The cells are therefore very compact and offer significant reductions in cell room area.

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

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

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

(d) Advantages/disadvantages of cell types

Diaphragm cells

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

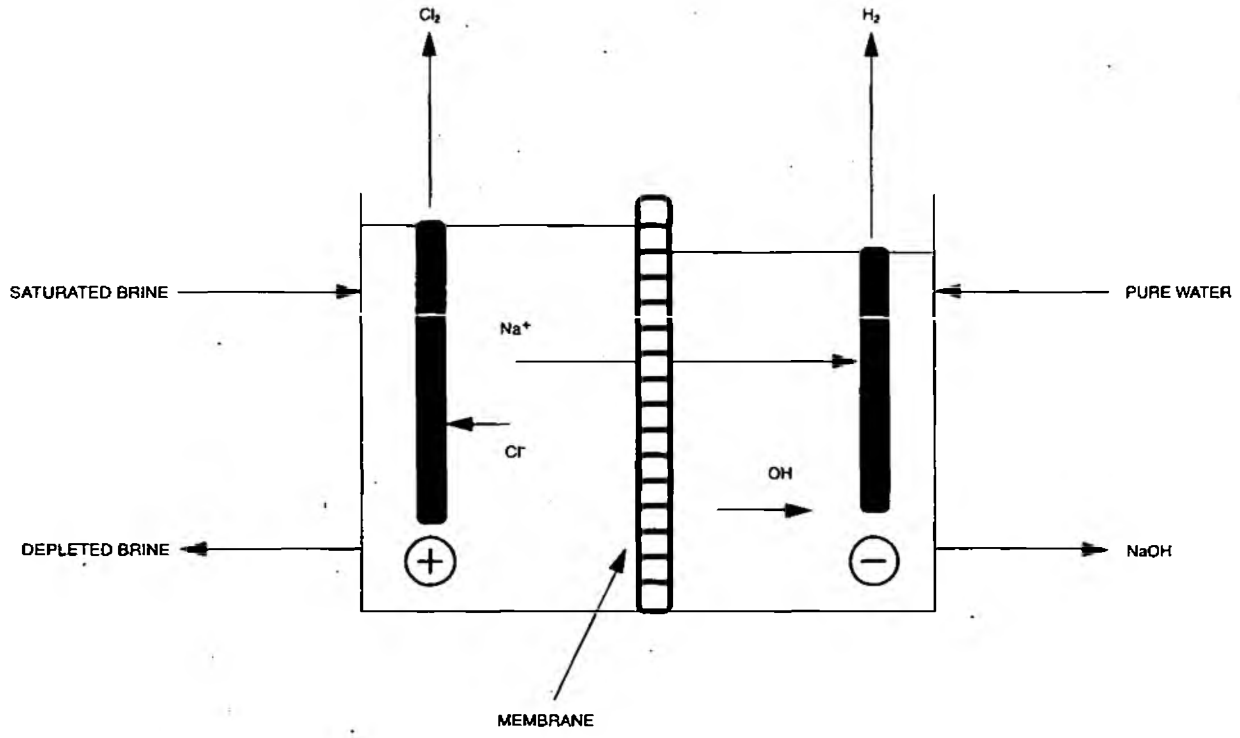
The asbestos diaphragm does degrade with operation and the resultant asbestos waste requires specialised handling.

Mercury cells

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

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

Figure 2.16 ***Simplified membrane cell***



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

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

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

Mercury cell operations and their routine replacement produce quantities of solid wastes, which must be regarded as mercury-contaminated. Each cell requires replacement every six years or so. Periodically the cell is drained and the bare cell is rinsed with hydrogen peroxide to remove, as Hg^{2+}, mercury that has amalgamated with the steel baseplate. Depending on the process, the total mercury lost as solids can be up to 24 g/tonne chlorine production. Mercury- contaminated solid wastes are landfilled.

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

Membrane cells

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

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

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

(e) Chlorine gas treatment

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

Cooling and drying

The drying of chlorine is accomplished by initial cooling of the gas from the cell. Excessive cooling should be avoided to preclude the production of chlorine hydrate. Sulphuric acid (96–98 wt%) is then used to reduce the moisture content to

Table 2.2 *Comparison of Electrolytic Cells*

	Advantages	Disadvantages
Diaphragm Cells	No mercury in products or wastes.	Poor performance during turn-down operation. Mixed product of dilute NaOH and brine requires further treatment and concentration, with significant energy use. Asbestos waste.
Mercury Cells	Proven and well-known technology. Insensitive to production upset conditions. Lower investment at higher current densities (CDs). Capacity increase at most existing plants by CD increase. No NaOH concentration required.	Products and wastes contain mercury. Higher energy use. Higher cell maintenance.
Membrane Cells	Produce high-purity, low-strength NaOH Reduced energy use. No mercury in products or wastes. More modern technology. Less maintenance. Easier operations.	Requires very pure brine feedstock. Higher investment. More sensitive to production upset conditions. NaOH needs concentration, increasing energy use. Need for higher level of plant personnel. Chlorine product can be contaminated with 2-3% O_2. Special materials of construction required.

less than 130 mg/m^3 in a series of contact towers. Waste acid is dechlorinated by air blowing and is normally sold, but may be reconcentrated for re-use or used for treatment of effluent. Chlorine produced from the sodium process receives similar treatment. However, owing to the presence of dust and fume the gas stream is first washed with a recirculating chilled water system comprising a spray tower followed by a packed tower. Solids in suspension are dealt with in an effluent treatment plant by pH correction and settling to remove suspended solids.

Compression, liquefaction and storage

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

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

Chlorine liquefaction is undertaken in condensers, which are arranged to allow liquid chlorine to flow to stock under gravity. The chlorine contains hydrogen, oxygen, nitrogen and carbon dioxide contaminants. These must be allowed for in the subsequent use of the gas as a process feedstock, or in avoiding explosive concentrations during liquefaction of the chlorine.

NOTE. Not all plants avoid explosive regimes. Some are designed to operate within these conditions, with vessels that are strong enough to withstand detonation.

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

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

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

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

Distillation

Chlorine is sometimes distilled to remove contaminants. Amongst these can be nitrogen trichloride, and highly chlorinated materials such as hexachloroethane, hexachlorobenzene and hexachlorobutadiene arising from traces of organic materials in the brine feedstock. These chlorinated heavy ends tend to be fully substituted and should be destroyed by thermal oxidation with recovery of hydrogen chloride. Detailed guidance is given in IPC Guidance Note S2 5.01 *'Waste Incineration'* (30).

(f) Hydrogen gas treatment

Strong hydrogen

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

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

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

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

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

Weak hydrogen

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

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

(g) Potential release routes

Releases to air

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

Releases to water

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

Releases to land

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

(h) Chlorine Production as a by-product

Production of sodium by electrolysis of fused salt

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

Production of magnesium by electrolysis of fused salt

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

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

2.4.3 Manufacture of bromine

(a) General

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

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

(b) Extraction from sea water

The sea-water process is illustrated in Figure 2.17.

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

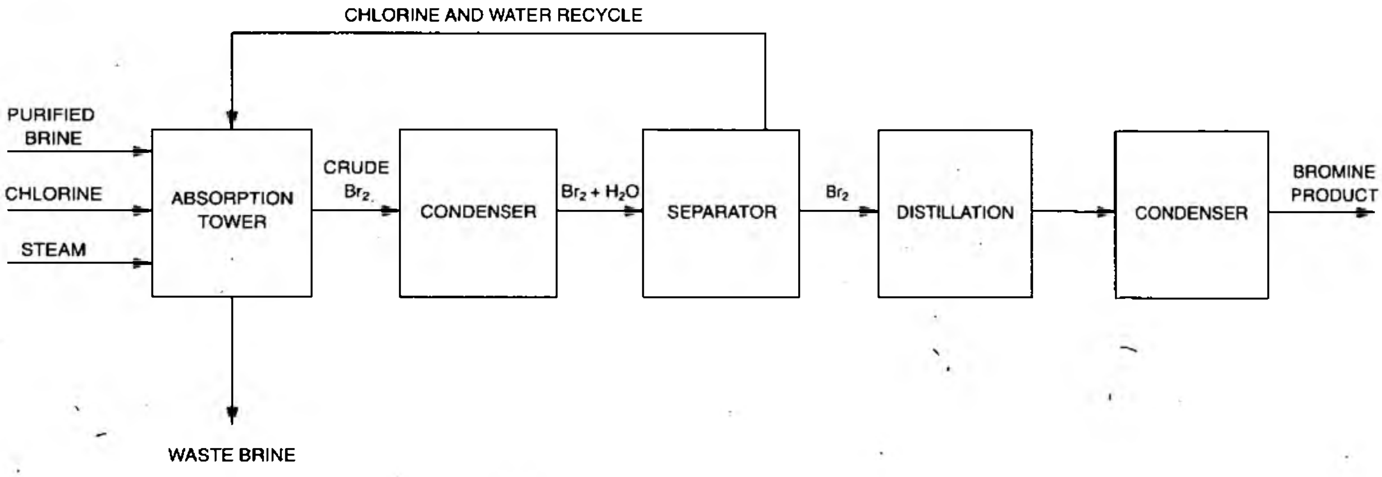
$$2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$$

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

The governing equation is:

$$Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$$

Figure 2.17 ***Bromine manufacture***



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

(c) Bromine loading and storage/chlorine storage

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

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

Imported liquid chlorine from tankers is off-loaded into stock tanks with similar facilities to those for bromine storage.

(d) Potential release routes

Releases to air

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

Releases to water

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

Releases to land

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

2.4.4 Manufacture of iodine

(a) General

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

(b) Potential release routes

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

2.4.5 Processes using or releasing halogens or halogen compounds

(a) Manufacture of lithium

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

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

Further information on sodium hypochlorite production is given in Section 2.4.5 (d).

Lithium chloride is generally manufactured on a batch basis by the addition of lithium carbonate powder to concentrated hydrochloric acid (34%). Effervescence results, with the carbon dioxide given off carrying over some hydrochloric acid spray.

The mixing tank is under slightly reduced pressure, resulting from the induced draught on the scrubber exhaust. Off-gases are scrubbed in a single-stage reinforced glass-reinforced plastic (GRP)/PVC-lined, packed scrubber, using dilute caustic soda.

Crystallisation of lithium chloride is effected by evaporation or spray drying.

Releases to air

- Chlorine and carbon dioxide from absorbers.

Releases to water

- Sodium chloride and residual sodium hydroxide in scrubber liquors.

Releases to land

- Spent eutectic (lithium and potassium chloride contaminated with a build-up of impurities) requires periodic disposal as 'special waste' to landfill.

(b) Manufacture of ferric chloride

Chlorine gas and hydrochloric acid are used in the batch manufacture of ferric chloride solution. Mild steel off-cuts are commonly used as the source of iron.

Ferrous chloride (10%) solution is made using fresh hydrochloric acid, spent pickling liquors (containing 2–3% hydrochloric acid) and steel off-cuts. Ferrous chloride (25 wt%) is added. This mixture is then reacted with gaseous chlorine, in a lined and lidded vessel, to oxidise the ferrous chloride to ferric chloride. Additions are regulated to produce a 43–44% solution.

In the continuous process, the plant comprises an iron dissolver, a packed ferrous tower and a packed ferric tower. Pickle liquor and dry chlorine are fed counter-currently, with the pickle liquor introduced into the ferrous tower and the chlorine into the ferric tower.

The reaction vessels are exhausted to atmosphere via a scrubber, with 10% ferrous chloride liquor being used as the scrubbing medium.

Releases to air

- Chlorine and hydrogen chloride from absorbers and ferrous towers.

Releases to water

- None.

Releases to land

- Sludges accumulating in reaction vessels are periodically disposed of, off-site, as 'special wastes' to licensed landfill.

(c) Manufacture of aluminium chloride

Aluminium chloride is made in a continuous process from aluminium metal and chlorine. Ingot aluminium is charged to a refractory crucible furnace in which it is melted (660°C). Dry chlorine is passed into the molten charge and forms aluminium chloride vapour. This reaction is exothermic and sufficient to melt further aluminium as it is introduced. External indirect cooling is also required. The aluminium chloride vapour leaves the furnace through a vapour duct, which passes to the air-cooled condensers.

Aluminium chloride crystals form on the condenser walls and are periodically removed (by vibrating the walls of the vessel), crushed, screened and packaged in moisture-tight containers.

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

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

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

Releases to air

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

Releases to water

- Caustic/brine/solution from catalytic treatment.
- Soluble aluminium compounds removed as hydroxides.

Releases to land

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

(d) Manufacture of sodium hypochlorite

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

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

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

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

The product must be maintained above pH 11, to minimise decomposition. Contact with heavy metals (Ni, Co, Cu, Fe) also catalyses decomposition. Hence materials used for plant and equipment are commonly high-performance plastics or rubber-lined steel.

Abatement

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

Releases to air

- Chlorine from absorbers.
- Hydrogen from electrolytic process.

Releases to water

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

Releasse to land

- None.

(e) Manufacture of phosgene (carbonyl chloride)

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

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

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

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

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

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

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

Residual gases may be burnt to convert phosgene to carbon dioxide and HCl. One advantage in this is that other pollutants, such as solvents and CO, will also be combusted. Combustion gases will, however, contain HCl and will require scrubbing. Detailed guidance on the avoidance of the formation of dioxins and furans is given in IPC Guidance Note S2 5.01(10).

Releases to air

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

Releases to water

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

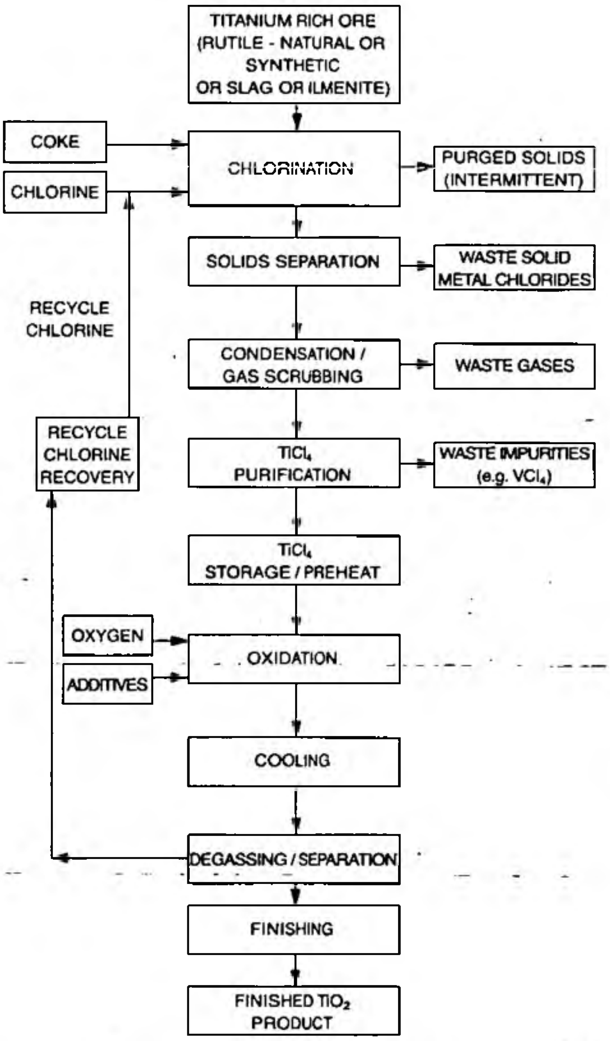
Releases to land

- catalyst from phosgene reactor.

(f) Manufacture of titanium dioxide by the chloride process

As stated in Section 2.2.7(a) titanium dioxide is also produced using the chloride route. Chlorine gas is used as an intermediary in the process and is recovered for re-use. The chloride process can treat a wider range of ores than the sulphate process including natural rutile (95% TiO_2), synthetic rutile (93–96% TiO_2) and lower-concentration ores. Higher-concentration ores are preferred to minimise chlorine losses, because impurities, such as iron in the ore feed result in a net loss of chlorine. Significant quantities of make-up gas are required.

Figure 2.18 *Outline flow diagram (Chloride process)*



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

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

$$2TiO_2 + 4Cl_2 + 3C \rightarrow 2TiCl_4 + 2CO + CO_2$$

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

$$FeO + Cl_2 + C \rightarrow FeCl_2 + CO$$

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

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

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

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

Oxidation

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

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2Cl_2$$

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

Absorption/desorption process

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

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

Chlorine recycle process

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

Abatement Systems for Gases

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

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

Currently, thermal converters are being installed to convert carbon monoxide in the tail gas to carbon dioxide, which reduces the toxicity of the discharge gases.

Abatement systems for liquids

Metal chlorides and coke from the reaction stage can be treated either by neutralisation with lime, resulting in metal hydroxide precipitates which are filtered and landfilled, or by converting these wastes into by-product hydrochloric acid and metal oxides. The conversion process involves roasting the metal chlorides in air to form HCl and leaving the oxide as a solid. Steam may be raised with a waste heat boiler. The process has potential for producing a relatively inert oxide with sales potential (as an inert filler). It also allows for recovery of the chlorine content of the wastes as hydrochloric acid (and hence chlorine value) if the acid is sold, not neutralised.

Abatement systems for solids

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

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

Releases to air

- Hydrogen chloride from absorbers.
- Chlorine from absorbers and storage tanks.
- Titanium tetrachloride from storage vents.

  NOTE. Normal practice is for vents from items of equipment to be manifolded to a vent header and drawn through an aqueous scrubber by an induced draught fan to atmosphere. Separate maintenance areas are ventilated via aqueous or caustic scrubbers.
- Carbon monoxide/carbon dioxide tail gas emissions to stack. (Percentage of monoxide to dioxide varies between 20 and 40%, unless thermally converted to CO_2).

Releases to water

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

Releases to land

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

(g) Manufacture of potassium iodide

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

$$3I_2 + 6KOH \rightarrow 5KI + KIO_3 + 3H_2O$$

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

$$2\,KIO_3 \rightarrow 2KI + 3O_2$$

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

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

Releases to air

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

Releases to water

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

(h) Manufacture of chlorine dioxide

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

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

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

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

Small-scale generation of chlorine dioxide

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

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

Abatement systems are typically those used for handling chlorine or its halides.

Releases to air

- Losses of chlorine dioxide from absorbers.

- Hydrogen chloride and chlorine.

(l) Interhalogen compounds

While a considerable number of interhalogen compounds are known to exist, their usage in general terms tends to be small. The exception is iodine monochloride, which is generated in situ for use in iodination reactions.

The pollution abatement techniques applicable are as for the individual halogens.

2.5 Hydrogen halides

2.5.1 Manufacture of hydrogen fluoride

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

(a) Process

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

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

- use of oleum to absorb excess moisture.

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

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

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

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

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

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

This will commonly include:

- scrubbed gases exiting from the kiln's emergency scrubbing system;

- gases from storage tank vapour spaces; and

- venting and purging occurring during tank filling and transfer operations.

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

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

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

(b) Potential release routes

Releases to air

- Particulates (losses from dust control equipment).

- Hydrogen fluoride from absorbers.

Releases to water

These will comprise combinations of:

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

Releases to land

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

2.5.2 Manufacture of hydrofluoric acid

(a) Process

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

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

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

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

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

(b) Potential release routes

Potential release routes into the environment associated with hydrofluoric acid manufacture are essentially the same as those for anhydrous hydrogen fluoride production.

2.5.3 Manufacture of hydrogen chloride

Anhydrous hydrogen chloride is obtained principally from the following sources:

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

(a) By-product hydrogen chloride

Chlorination of hydrocarbons

Hydrogen chloride is produced as a by-product of substitution reactions. (Refer to IPCGN S2 4.02(21) for further details).

Thermal cracking

Dichloroethane (DCE) is converted to hydrogen chloride and vinyl chloride monomer (VCM) by passing through heated tubes followed by a DCE quench to stop the reaction selectively at the optimum VCM make. Hydrogen chloride is separated by distillation and refrigeration to produce anhydrous liquid hydrogen chloride for sale, or for use in oxychlorination reactors to make further DCE. These processes are described in more detail in IPCGN S2 4.01(20).

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

Releases to air

- Hydrogen Chloride from absorbers.

Releases to water

- Scrubber effluents.
- Catalyst from reactors.

Releases to land

- None.

(b) Combustion of hydrogen and chlorine

This particular manufacturing operation is often carried out as an ancillary process to the manufacture of chlorine (see Section 2.2). There is thus the potential for carry-over of contaminants from the previous manufacturing operation, eg mercury from the chlor–alkali process.

So-called synthetic hydrogen chloride is made by burning chlorine in an excess of up to 20% of hydrogen in proprietary carbon burners. A graphite bursting disc, relieving to stack in case of explosion, is provided.

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

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

(c) Evaporation of 36 wt% hydrochloric acid

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

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

Releases to air

- Hydrogen chloride from absorbers.
- Excess hydrogen.

Releases to water

- Sodium chloride in spent absorber liquors.

Releases to land

- None.

2.5.4 Manufacture of hydrochloric acid

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

2.5.5 Manufacture of hydrogen bromide

Commercial anhydrous hydrogen bromide is obtained principally from three sources:

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

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

(a) Combustion of bromine and hydrogen/catalysed reaction of bromine and hydrogen

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

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

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

The exit gases (hydrogen bromide and a small amount of residual hydrogen) are then cooled and pass to plants using the AHBr or to absorbers, producing hydrobromic acid.

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

(b) Potential release routes

Releases to air

- Hydrogen bromide and bromine losses from absorbers. NOTE. Normal practice is to recover hydrogen bromide in aqueous scrubbers to produce hydrobromic acid in strengths up to 47 wt% - the binary azeotrope contains 47.5 wt%, with residual gases vented via a caustic scrubber.
- Excess hydrogen.

Releases to water

- Sodium bromide and sodium hydroxide in spent absorber liquors.

Releases to land

- Spent catalyst.

2.5.6 Manufacture of hydrobromic acid

(a) Process

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

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

(b) Potential release routes

Releases to air

- Hydrogen bromide and traces of organics from absorbers.

Releases to water

- None.

Releases to land

- None.

2.5.7 Use and release of hydrogen halides and their acids

The following are examples of processes not covered by other guidance notes in this series.

(a) Friedel–Crafts processes

Two organic feeds (one chlorinated) are reacted in the presence of an aluminium chloride or ferric chloride catalyst. Chlorine from one of the organic feeds is substituted and evolved as hydrogen chloride. Any acidic vapour given off during the reaction is scrubbed before being vented.

Friedel–Crafts reactions are generally carried out between 40 and 90°C at atmosphere pressure.

Once the reaction is complete, the mixture is quenched in water or a weak solution of hydrochloric acid. The quenched mixture is treated further.

The final stage of the process may require purification of the product using for example, distillation.

(b) Alternative Friedel–Crafts Catalysts

These consist of restructured montmorillonite clays. Metal ions are then incorporated into the structure to provide Lewis acid characteristics to the clay, superimposed onto its normal properties. These catalysts differ fundamentally from conventional Lewis acids in that their action is heterogeneous and truly catalytic.

Chemicals such as benzophenone may be manufactured using a novel Friedel–Crafts catalyst.

The process minimises evolution of hydrogen chloride, since it is not produced from the catalyst (in contrast to the standard aluminium chloride route). Furthermore there is no need to quench the reaction product in water using this route, and thus additional aqueous effluent is prevented.

(c) Manufacture of methyl chlorosilanes/siloxane polymers

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

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

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

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

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

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

Releases to air

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

Releases to water

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

Releases to land

- Sludge from the effluent treatment plant.

- Spent neutralised reaction mass.
- By-product solid siloxanes.

(d) Manufacture of sodium bromide

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

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

Releases to air

- Hydrogen bromide from absorbers.

Releases to water

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

Releases to land

- None.

(e) Other processes involving hydrogen halides

Other typical processes using or releasing hydrogen halides are covered in other guidance notes in this series.

IPCGN S2 4.02(21) covers, for example, use of halogens in solid and liquid organic chemical processes.

A typical off-gas stream from such a reaction contains a mixture of halogen, hydrogen halide and organic material carried over.

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(23), reports;
- BAT Review Reports on Pollution Control;
- HMIP Technical Guidance Notes; and
- Environmental Technology Best Practice Programme (ETBPP)(24) Good Practice Guides.

These techniques need to cover releases from raw materials reception/storage, internal transportation, processing, waste materials internal transport and 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 the Inspector should be looking for 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.

Prevention, minimisation and recycling/re-use procedures(25) should be applied whenever possible, within the criteria for BATNEEC and BPEO.

The Inspector should be satisfied that an applicant has reviewed all available options and has demonstrated that the selected combination of primary process and abatement equipment represents BATNEEC, and that the concept of BPEO is satisfied.

In general, pollution control equipment should be kept running during start-up and shut-down for as long as is necessary to ensure compliance with release limits in Authorisations.

All plant and equipment should be subject to regular preventive maintenance programmes, in line with operational requirements, to ensure continued optimum performance.

More details of the methods available for preventing or reducing releases are listed in Research Report No P200(26). The most important techniques include, but are not restricted to, those given below.

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(27). 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'(28) or similar initiatives provide a good framework for the implementation of management techniques. The key aspects of this Initiative, to which companies should be committed through their senior management, and which they should be able to demonstrate they are applying, are the following:

- 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 work with authorities to develop and implement measures where needed.
- Employees and contractors are aware of the commitment and are involved in its delivery.
- 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 defined 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 dependent 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 as a result of 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 (25), 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.
- There should be a clear statement of the skills and competencies required for each job.
- 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 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

The aim should be to maximise material recovery, and minimise releases, by applying appropriate techniques. 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.

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(29) for large combustion plant and S2 5.01(30) 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.

Processes must be operated in such a way as to protect the environment as well as persons at work. 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 over-pressurised.

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:

- 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.

Some compounds have low odour thresholds. Therefore, the control of odours should be an integral part of 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. The selection of refrigerant to chill and liquefy chlorine gas has significant environmental implications. Refrigerants with significant ozone depletion potential such as CFCs should be replaced with non-ozone-depleting refrigerants. 'Transition' refrigerants such as HCFCs should also be replaced in the longer term. Refrigerants that are removed must be sent to an authorised operator for destruction.

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

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

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.

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.
- Limitation of the flow of the input reactant such that the heat of reaction evolved cannot exceed the capacity of the reactor cooling system.

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.

3.3.2 Particulate matter

Solids handling includes discharging solid raw materials, conveying them to process, discharging, storing and conveying solid products and packing. 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.

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.

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, that this effect has been minimised at source, and how the dust is to be removed.

The methods available for minimising or reducing discharges of particulate matter to the atmosphere may include the following used on their own or in combination:

- cyclones;
- fabric filters;
- high efficiency particulate arresters (HEPA);
- ceramic filters;
- wet collection devices;
- electrostatic precipitators – both wet and dry; and
- dust suppression equipment.

Further information is available in Technical Guidance Note A3(11).

The appropriate technique depends on the size and other physical and chemical characteristics of the particles, the loading, the carrier gas stream process factors such as temperature and allowable pressure drop, and operational factors including space limitations such as floor area 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 5µm; smaller particles down to about 0.5µm can be separated where agglomeration occurs. High-efficiency cyclones are capable of removal efficiencies of the order of 90% for particles down to 5µm.

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 20µm. 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 are particularly useful as secondary or tertiary gas cleaning devices with a cyclone or dry scrubber located upstream.

Filter efficiency may be enhanced by pre-coating the filter cloth.

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.

It is unlikely that bag filters can be used at high temperatures because of the temperature limit of the bag filter material.

Regular maintenance and cleaning of the filters is necessary to maintain removal efficiencies and limit pressure drops.

Cleaning can be achieved by a reverse jet of air, needing the filter to be off-line for the cleaning cycle, hence requiring a bank of filters to achieve continuous abatement of particulates.

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. Suitable fabric filters may therefore attain many of the new plant emission levels, although on some applications a back-up device such as a HEPA filter (see below) may be necessary, eg where a significant proportion of the particles is below 1µm diameter.

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 by using differential pressure transmitters or manometers.

(c) High-efficiency particulate arresters

HEPA filters exist in several forms and self-cleaning versions have been recently introduced. Generally the filters consist of a bed of densely packed fibres 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 used, HEPA filters are capable of achieving high removal efficiencies for particles of 0.5µm diameter and larger. They can also remove a significant proportion of particles down to 0.01µm 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 may 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 sub-micron 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 sub-micron 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 sub-micron particles the upper range of the pressure drops (1500 mm water gauge) may be required, particularly if better than 99% collection efficiencies are required.

The 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 0.01µm 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 ESP has the advantage of being a low-pressure-drop device; however, it has the disadvantage of the risk of sparking off explosions of flammable gas mixtures. This limits the application of electrostatic precipitators where flammable gases may be present. The ESP may also be less suitable for control of particulates if the electrical resistivity of the dust is high and/or is very variable.

(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.

A silicone spray may be utilised to suppress the dust from some stockpiles.

3.3.3 Gaseous abatement techniques

Because of the nature of the gaseous substances likely to be released from the processes covered by this Guidance Note, absorption is likely to be the main effective abatement option and further discussion is restricted to this technique.

(a) Absorption – general comments

Where a soluble gas is released from a process and needs to be abated before release to the atmosphere, this is usually achieved by scrubbing in a wet scrubber. This technique 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 detailed in Section 3.2.2(e) 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, eg by using an appropriate raw material or solvent as the absorbent to recover solvent or partially reacted products such that they can be recycled to the process, or used elsewhere, 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. Hence the water treatment plant should be an adequate size to cope with any added discharge. 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.

(b) 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 systems.

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

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

Where a scrubber is used for odour control, the absorbent is often a suitable oxidising agent.

(c) 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.

Spray towers can also be used for the removal of particulates. Specialist spray scrubber designs, using high pressure liquor, can treat gases to plate tower standards without fouling or solids blockage problems.

Spray towers or spray dryers may also be used as semi-dry scrubbers to abate gases and particulates with slurries sprayed into the tower. The heat of the gases evaporates the water in the slurry and provides a solid waste with the contaminants absorbed into or onto the solid waste.

(d) Wet mop scrubbers and rotaclones

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

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

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 Chimney and vent plumes

Releases from vents and chimney stacks 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 to 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 Dispersion from chimneys and vents

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(4).

For major sites it is considered BAT for dispersion modeling to be carried out that 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. Inspectors should expect operators (or relevant experts acting for them) 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 (9, 10) 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), the Inspector should require a new dispersion model to 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(9).

3.3.7 Odours

Substances present in emissions to air, which are known to be odorous, should be identified and quantified. Techniques described in this Note should be employed to ensure that they are minimised to prevent them being noticeable outside the site boundary. Carbon adsorption and other types of odour-adsorbing material can be utilised in the abatement of odours.

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 may contain dissolved heavy-metal compounds including sulphates and fluorides as well as suspended solids.

The following techniques should be considered for reducing 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.
- Recycle waste water back to the process or to secondary uses such as equipment wash-down, using water pinch analysis if applicable.
- Employ indirect contact heat exchange devices.
- Use improved control and optimised operating conditions.
- Segregate process water, storm water and indirect cooling water streams to reduce the hydraulic loading to waste-water treatment equipment or sewers.
- Develop spill contingency procedures to minimise the risk of accidental release of raw materials, products and waste materials and to control such spillages so as to prevent their entry into water.
- Shelter bunded areas to prevent transfer of pollutants to storm 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 solid dosage forms. Vacuum extraction reduces the loss of

product to the waste water and in some cases allows the recovery of these products.

- Wipe down equipment that is accessible rather than washing and rinsing it.

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(32).

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.

A site-specific spillage contingency plan should be prepared.

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, primarily to remove inorganic compounds.

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, 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 sewer to treatment plants in a closed system as far as practicable. The sewer should be designed to prevent leakage into ground and to prevent ingress of groundwater.

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(33).

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(34) gives some guidance), or fire fighting-foams. Emergency storage lagoons may be needed to prevent contaminated fire water reaching controlled waters(35).

(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(16) and ETBPP guides(24).

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.

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^3/day effluent) are likely to carry out basic treatment before discharging the effluent to a sewerage undertaker. Often inorganic acid plants are part of a much larger chemical plant, in which case the effluent from the inorganic acid plant would be directed to a site-wide effluent treatment facility.

(a) In-plant treatment

Effluent balancing is of importance to the waste-water treatment plant, but often not emphasised enough. The balancing of waste waters prior to entering the plant will help prevent excursions from being caused by process plant upsets.

- For heavy metals, combinations of: oxidation/reduction; precipitation; filtration; ion exchange.

(b) Primary treatment

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

- Neutralisation.
- Coagulation/flocculation.
- Flotation/sedimentation/filtration.

(c) Secondary/tertiary treatment

A number of methods may be applicable:

- Chemical precipitation.
- Electrolytic exchange.
- Ion exchange.
- Membrane techniques.
- Reed beds.

(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:

- 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.

3.4.4 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 a suitable retention time for dosing.

Where large discharges of effluent with high or low pH are possible, consideration should be given to a two-or three-stage feed-forward pH control system.

Care should be exercised when acid-dosing effluent in case toxic gases are released, eg chlorine from hypochlorite solution or hydrogen sulphide from sulphides. 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.

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.

The neutralisation of an acid waste with an alkaline waste should be considered if compatible streams are available.

3.4.5 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.

(a) Settlement

Separation of up to 90% of the suspended solids can be achieved by settlement.

Settlement is carried out in a clarifier. The clarifier design that is considered to be the most efficient and economical is a circular, mechanically scraped tank. However, depending on the flowrate, one or more pyramidal-type settlement tanks may be appropriate.

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

(b) 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^3/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. 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.

(c) Precipitation

Precipitation is the most widely used technique for removal of certain compounds that could be recycled or are more appropriately disposed of to land than water.

Control of pH, solid particle growth conditions and residence time are some of the key parameters to be considered.

The use of an appropriate precipitation technique is the most common method encountered with dissolved metal compounds. Metallic species are likely to be more mobile at acidic conditions and therefore raising the pH to typically between pH 8 and 10 will be required to precipitate them. Care is required in the choice of optimum pH for mixed waste streams. In some instances more than one precipitation stage may be required to effect the required level of precipitation.

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.

Hydroxide precipitation is the most frequently used technique to remove the metal species from aqueous waste streams. It relies on the low solubility of heavy-metal hydroxides in water, which 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.

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. An alternative which should be considered where applicable is the use of magnesium hydroxide in slurry form; this 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.

Carbonate precipitation by the use of sodium carbonate or carbon dioxide may be an appropriate method in some cases, eg streams containing nickel compounds.

Separation of precipitates is described below 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.

(d) 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.

(e) 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, 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. 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.

(f) Electrolytic exchange

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

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

3.4.6 Activated carbon adsorption

Activated carbon columns can be used for the removal of low concentrations of metal species, for instance to polish a final effluent to provide recyclable water.

Activated carbon adsorption is likely to be encountered infrequently in processes covered by this Guidance Note and is not discussed further.

3.4.7 Ion exchange resins

Ion exchange can be employed for the removal of undesirable anions and cations from a waste water. Cations are exchanged for hydrogen or sodium, and anions for hydroxyl ions.

Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Ion exchange resins are called cationic if they exchange positive ions and anionic if they exchange negative ions.

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

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

3.4.8 Membrane processes

Membrane processes include: ultrafiltration, reverse osmosis, membrane filtration and pervaporation. The efficiency of a filtration process 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. This is determined greatly by the amount of solids present in the stream to be cleaned.

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

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 and preferably better than other available techniques.

3.5 Minimisation of waste to land

3.5.1 General

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, 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.

Packaging should be reduced to the minimum necessary in cooperation with suppliers of products brought on to the site.

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.

Ion exchange resins and catalysts 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.

As much of the sludges as practicable should be recycled for processing (eg by filtration, centrifuging, etc) to minimise the amounts requiring disposal.

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.

All wastes should be stored in appropriately identifiable and suitably designed and protected containment areas and equipment pending their transfer to on- or off-site disposal facilities.

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(37).

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.

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(19) as noted in Section 1.5.8 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*(18), 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

The benchmark release levels to air are summarised by substance and process sector in Table 4.1.

Table 4.1 ***Benchmark releases to air (mg/m^3)*** $^{(a)}$

Substance	Process sector				
	Sulphuric acid	**Sulphuric acid from smelting**	**Nitric acid**	**Halogens**	**Hydrogen halides**
Ammonia			<10	15	
Bromine				10	10
Carbon monoxide	100	100	100	100	100
Chlorine and oxy cpds as Cl_2				10	10
Fluorine and cpds (as HF)				5	5
Hydrogen bromide			5	5	5
Hydrogen chloride	b		10	10	10
Hydrogen fluoride	b		5	5	
Hydrogen iodide			5	5	5
Hydrogen sulphide	5	5	5		
Iodine				10	
Mercury				0.1$^{(g)}$	0.1$^{(g)}$
Oxides of sulphur (as SO_2)	150 $^{(b-e)}$	350			
Oxides of nitrogen (total acid forming as NO_2)	300	300	200		
Nitrous oxide			200 $^{(f)}$		
Particulate matter	20	20	20	20	20
Phosgene				1	1
Phosphorus and cpds (as P)				1	1
VOC total Class A $^{(h)}$	20	20	20	20	20
VOC total Class B $^{(h)}$ (as toluene)	80	80	80	80	80

a The reference conditions applicable to these 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 Note S2. 1.01$^{(29)}$ for large combustion plant and S2 5.01$^{(10)}$ for chemical waste incineration, for information relating to release levels.

b For acids handling plant (reconcentration and purification processes) certain parameters will depend on the chemicals handled by individual sites.

c Emission level is achievable using double absorption, a 'low-bite' catalyst and tail end abatement of the process exhaust gases.

d Emission level is achievable by using single absorption and tail end abatement.

e During start-up, much higher releases can be experienced. Procedures should be used to limit the maximum sulphur losses to the levels indicated below. These values apply only to the first 5 hours of operation. The onus is on the operator to improve the start-up procedures and minimise the environmental impact of the plant.

Maximum sulphur loss (%)	**Steady state**	**Start-up**
New plant	0.05	2.0
Existing double adsorption plant	0.5	2.0
Existing single adsorption plant	2.0	3.0

The manufacture of titanium dioxide is subject to EC Directive 92/112/EEC(17) which gives the following limits:

Substance	**Limit (mg/Nm^3)**
Chlorine - chloride route (daily average), (at any one time)	5 40
Oxides of sulphur – sulphate route (as SO_2)	10 kg/tonne of TiO_2 produced
Particulate matter (main sources)	50
Particulate matter (minor sources)	150

f Where NSCR is used.

g PARCOM Decision 90/3 of 14 June 1990(15) relates to Reducing Atmospheric Emissions from Existing Chlor–Alkali Plants, as follows.

Contracting Parties to the Paris Convention on Marine Pollution from Land Based Sources AGREE:

- that existing mercury based chlor-alkali plants shall be required to meet a standard of 2 g Hg/tonne of chlorine capacity for emissions to atmosphere unless there is a firm commitment that the plant will be converted to mercury-free technology by the year 2000;
- that mercury in hydrogen which is released to the atmosphere, or is burnt, is to be included in this standard;
- and RECOMMEND that existing mercury cell chlor-alkali plants be phased out as soon as practicable. The objective is that they should be phased out completely by 2010.

h 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/h
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

The benchmark release levels to surface water are summarised in Table 4.2.

Table 4.2 ***Benchmark releases to water (mg/ℓ)*** [(a)]

Substance	
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)	50–100
Ammoniacal nitrogen (as N)	1–5
Suspended solids (dried @ 105°C)	20–30
Cadmium (expressed as cadmium)	0.01 [(e)]
Mercury (expressed as mercury)	0.005 [(e)]

a The levels given here are ranges achievable after effluent treatment using a biological treatment step and are not release limits. They are given on the basis of 95% of values not exceeding the relevant level.

b For titanium dioxide production, EC Directive 92/112/EEC (17) gives limits for releases to water:

Substance	Limit (kg/tonne TiO_2 produced)
Weak acid waste, treatment waste and neutralised waste from chloride process (total chloride Cl^-)	130 using neutral rutile 228 using synthetic rutile 450 using slag
Weak acid waste and neutralised waste from sulphate process (total sulphate SO_4^{2-})	800

c For chlor–alkali plants, EC Directive 82/176/EEC(16) gives the following release limits for mercury to water:

Process type	Monthly average limit not to be exceeded	Application
Recycled brine – grams of mercury per tonne of installed chlorine production capacity	0.5	Applicable to the mercury present in effluent discharged from the chlorine production unit.
Waste-water discharges – grams of mercury per tonne of installed chlorine production capacity	1.0	Applicable to the total quantity of mercury present in all mercury-containing water discharged from the site of the industrial plant.
Lost brine – grams of mercury per tonne of installed chlorine production capacity	5.0	Applicable to the total quantity of mercury present in all mercury-containing water discharged from the site of the industrial plant.

d 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.

e Statutory Instrument (1989) No 2286 (11) 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 cost. 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, also known as sector affordability, 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.

Set out below is a summary of the assessment of the economic and financial climate and status of the inorganic chemicals industry, as at 1998, as well as the information concerning abatement techniques against which the application of BAT and BATNEEC may be judged.

5.2 The UK inorganic chemical industry structure and market

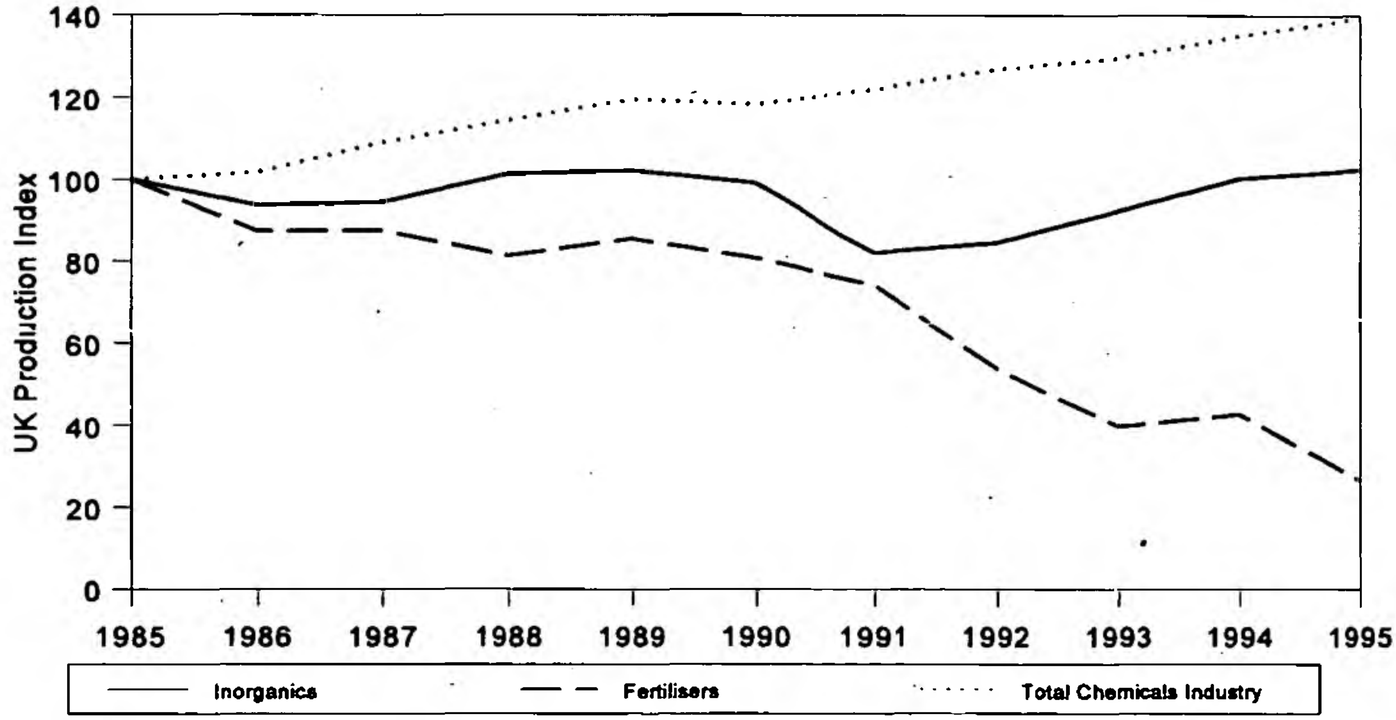
5.2.1 UK inorganic chemical sector as a whole

(a) Market overview

The UK inorganic acids and halogens industry comprises a wide range of companies, some large and providing integrated facilities, some small with a range of specialist products. Generally, inorganic chemicals are not viewed as a growth sector compared to some parts of the chemical industry, eg plastics and pharmaceuticals. Figure 5.1 shows how both the inorganic and fertiliser chemical outputs have declined in recent years, compared to total chemical output. Data from the Chemical Industries Association shows that, taken together, the inorganic and fertiliser sectors are expected to represent 13% of total UK chemical investment during the period 1997–99. The Government last reviewed the UK inorganic chemical industry in 1987 in a NEDO (National Economic Development Office) report entitled *Chemicals: A Positive Future*. According to the report, the key determinants for development of the UK inorganic chemical sector would be as follows:

- Competitive energy prices for large, intensive users.
- Exchange rate/interest rate stability at a reasonable level.
- Recovery of the UK's manufacturing base.

Figure 5.1 *UK production of inorganics, fertilisers and all chemicals*



In the past five years there have been major changes in the structure and ownership of the UK and international chemical industry. Producers with manufacturing assets in the UK, as elsewhere in Europe, are increasingly looking at the international competitiveness of their products. Producers with growth products are looking to see whether existing and future UK-based production can form part of a global production strategy.

The chemicals covered by this Guidance Note are categorised into one of four types: commodity, speciality, growth or mature chemicals.

(b) Commodity chemicals

Commodity chemicals (eg nitric acid, sulphuric acid, chlorine) are large-volume, low-price products for which the chemical business cycle is a key economic fact of life. The chemical business cycle is the period of time (usually between 5 and 10 years) between two peaks in chemical industry profits. The last two peaks in profits for the overall Western European chemical industry were in 1989 and 1995 so the cycle lasted six years. The average profit margin for Western European chemical companies throughout the last chemical business cycle was between 2 and 5% of sales value (turnover) according to an industry source.

(c) Speciality chemicals

Speciality chemicals are the opposite of commodities. They are low-volume, high-price chemicals usually characterised by high demand growth. Also companies usually achieve higher margins on speciality chemicals. Investment for speciality chemicals can occur at any time irrespective of the general chemical industry cycle. Examples of these are sulphites, iodates and oleum.

(d) Growth chemicals

Growth chemicals (eg phosgene), are those non-specialities for which demand is expanding faster than overall economic GDP. Where demand is growing at rates of 2–5 times GDP, these products are described as 'high growth'. These are the 'rising stars' of today, which will become commodities in 10–20 years' time. Producers with high- growth products will be most concerned with the speed of new plant investment and will be planning 5–10 years ahead.

(e) Mature chemicals

Mature chemicals (eg ferric chloride, sodium hypochlorite) are those for which demand is either falling in volume terms or where growth is less than the overall GDP growth rate in the national economy. These tend to be old products, gradually becoming obsolescent as newer products expand their market share. Producers with mature products may well be most concerned with cost reduction in order to maintain profitability in the absence of growth.

(f) Financial results

All companies operating in these industries are public or private limited companies returning annual accounts to Companies House. Important financial ratios that indicate the state of a company's operations are:

- Return on capital for the whole company can be calculated from information in the annual report and is shown on the figures in the text. Return on capital is the company's annual profit expressed as a percentage of all capital employed by the company including manufacturing plant (depreciated), working capital and other overheads for all the company's activities.
- Return on investment (ROI) is applied to an individual manufacturing plant and is its annual profit expressed as a percentage of the plant investment cost. This simple ROI therefore requires estimates or data for, product selling price, feedstock costs, plant investment costs and operating costs. ROI in this case excludes the cost of financing, provision for plant depreciation and tax.

Based on the current financial climate of these industries, typical figures for these financial ratios have been compiled below for each of the main production processes. It should be noted that percentage figures given in the text that follows for simple ROI are for a new plant. For an existing fully depreciated plant, a higher rate of return can be expected based on similar assumptions to those for new plant.

With regard to access to external financing, it is noted that, for the chemicals industry generally, the corporate finance borrowing cycle is 180 degrees out of phase with the capital investment cycle.

(g) Economic outlook

For each industry subsector a view of likely future economic performance is presented in the text that follows based upon all the economic and financial data available. In recent years the economic performance of these subsectors has been reasonably good by historical standards. This is expected to continue until the next cyclical downturn in the chemicals industry.

5.2.2 Sulphuric acid and related industries

(a) Market overview

The current UK market for sulphuric acid is estimated at about 1500 ktpa, mainly in concentrated form. This represents a sizeable fall from the 4000 ktpa market size of the 1980s and is mainly due to the decline of UK fertiliser manufacture, lower steel production and more efficient use of the acid. The overall number of sulphuric acid manufacturers in the UK has also continued to decline. The remaining companies produce acid from some of the oldest chemical sites in the UK and represent a mixture of interests from broad-based bulk chemical production to specialist acid producers and non-ferrous metal manufacture.

In the UK, most production is tied to other industrial operations or is recycled acid after reconcentration. The average size of UK plants is about 500 tpd compared to 3000 tpd plants in the USA and 1000 tpd plants in continental Europe. In addition, the continental European producers have spare export capacity.

(b) Reported prices

From the information available, neither feedstock nor product prices have had a significant effect on the sulphur industry profitability in recent years.

(c) Financial Results

Recent financial results for a typical sulphur-based inorganic chemical company are shown in Figure 5.2. The trends of all four financial parameters appear to track the overall UK chemical industry business cycle, ie recession in the early 1990s, a strong recovery in 1994 rising to a peak in 1995.

A current return on investment for a typical sulphuric acid plant (of about 330 ktpa capacity produced by the sulphur combustion process) is estimated to be 20%. This is an acceptable return, indicating a reasonable balance in the market for feedstock supply and product demand.

A typical company in this sector would be larger than the average chemical company in the UK and would have a credit rating of above average for UK industry as a whole.

(d) Economic outlook

Sulphuric acid is a mature commodity and there is little evidence to suggest major economic changes in the UK industry in future. Prospects for sulphuric acid recovery almost certainly improved in 1996 because of the introduction of a UK landfill tax, which improves the relative economic attractiveness of recovery versus disposal. Another spent acid concentration plant for the UK has been mooted.

5.2.3 Nitric acid and related industries

(a) Market overview

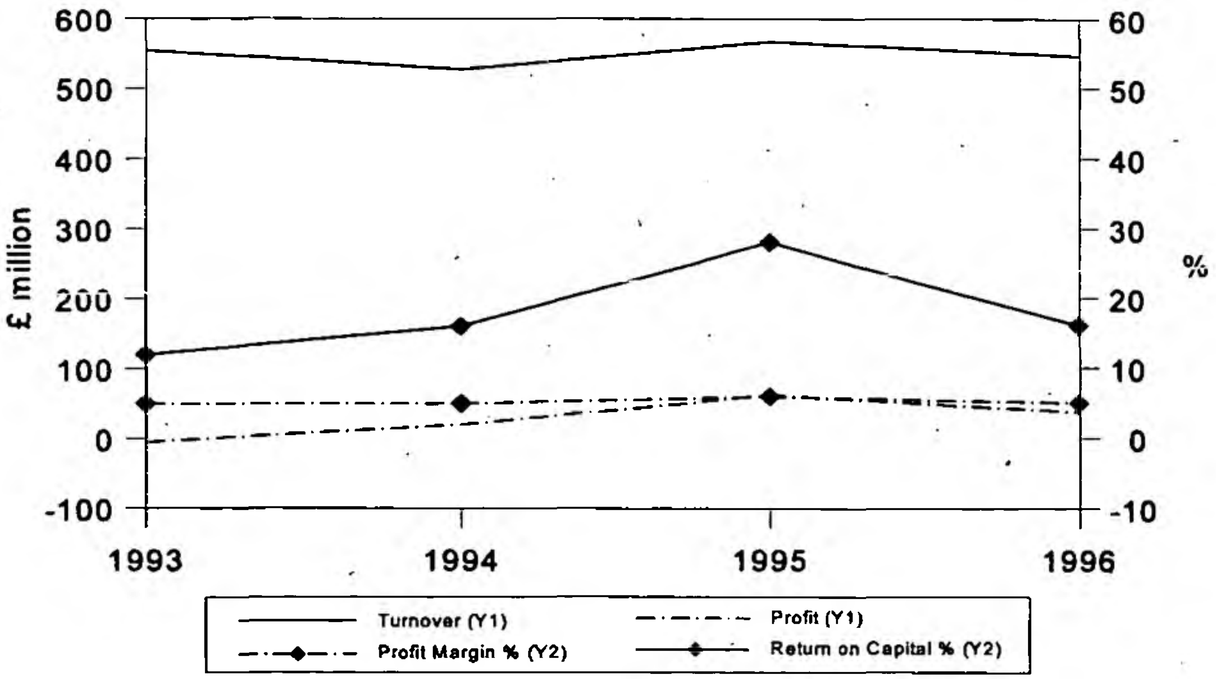
The nitric acid industry is about one-third the size of the sulphuric acid industry in the UK. Most weak nitric acid is used captively, while most concentrated acid is for merchant sales. In 1997 the major UK nitric acid producer sold its fertiliser business to an American company and most UK nitric acid production is now foreign-owned.

Most UK output is used to manufacture fertilisers (ammonium nitrate granules). Other significant uses are in the manufacture of polyurethanes, fibres, explosives and the treatment of metals.

Fertiliser markets

Western European fertiliser production and consumption have declined by about 25% since the end of the 1980s. The markets suffered a disastrous slump in 1991–2. Western European demand was declining slowly but, following the break up of Comecon in 1990, the FSU and Eastern Europe doubled their exports of fertilisers to the West. This is having a major impact on prices and on production in Western Europe. Western Europe responded by closing down 25% of capacity and making 50% of the workforce redundant.

Figure 5.2 ***Inorganic sulphur-related manufacturers – typical financial results***



Now the European fertiliser environment is stabilising and the oversupply situation is improving (see IPCGN S2 4.04[8] for further detail).

Chemical markets

Demand for concentrated nitric acid for high-growth chemical production is generally increasing.

(b) Reported prices

Significant changes have occurred recently in the price of ammonia feedstock used to make nitric acid. Ammonia prices have fluctuated around £250 per tonne, which is high compared to historical price trends, which are closer to £150 per tonne. More recently they have fallen back towards the lower level. Ammonia is a bulk chemical commodity for which price fluctuations are expected by industry.

(c) Financial results

Recent financial results for a typical nitrogen-based inorganic chemical company are shown in Figure 5.3. The trends show that losses in 1993 have been turned into profits in recent years up to the start of 1998.

One producer saw 1996 profits in its agro-business unit increase by 14% on a 3% rise in sales.

Another company says that its finances were highly geared (high debt/equity ratio) in early 1990s, but after initiating a drastic cost-cutting programme it is now in a growth phase and is expecting to invest.

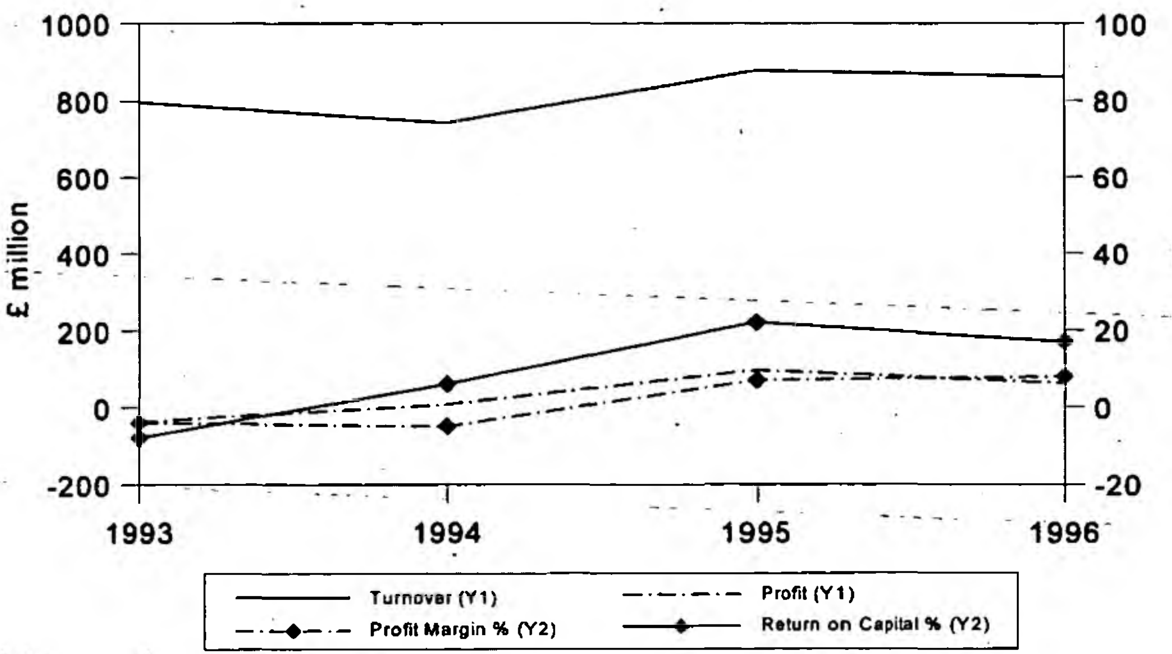
A current return on investment for a typical nitric acid plant (of about 170 ktpa capacity) is estimated to be 40%, which is high. A recent consultants' report also indicated a very high return on investment for a particular process selected. A typical company in this sector would be larger than the average chemical company in the UK and would have a credit rating of above average for UK industry as a whole.

(d) Economic outlook

The economic prospects for weak nitric acid are tied to those of the fertiliser industry. After a long period in the doldrums in the early 1990s, the outlook for European fertiliser producers has improved. Positive features are the reduction in EU set-aside land, recovery in domestic demand in Eastern Europe/FSU and the near-total lack of investment for 10 years which has helped to reduce overcapacity. However, not all the problems have been dispelled. Nitrate pollution is still a major issue, greater European use of urea fertiliser would not require nitric acid, exports to non-European markets are generally uneconomic, and the German market has been almost totally lost to Eastern European suppliers.

The prospects for concentrated nitric acid are related to a larger number of industries. There is no evidence that UK production of stainless steel will dramatically increase, so nitric acid demand for pickling is unlikely to rise. Metal brightening/anodising is likely to increase in the UK particularly for aluminium components for the automotive industry. Of the chemical uses, the UK is expected to increase production of high-growth MDI polyurethane intermediate. Overall, production of concentrated nitric acid in the UK is likely to remain comparatively stable in the medium term.

Figure 5.3 *Inorganic nitrogen-related manufacturers – typical financial results*



5.2.4 Inorganic halogens industries

(a) Market overview

Chlorine

Chlorine is a large-volume commodity chemical for which prices fluctuate widely. The chlorine production business is cyclical (recently 8–9 year cycles) and relies on brief periods of high profits for plant investment.

One feature of the industry is that chlorine is always co-produced with equally valuable caustic soda, and historically, when the price of one chemical is high, the price of the other is usually low. In this way the chlorine producer (or more strictly the chlor–alkali producer) is partly cushioned from the financial effects of the big fluctuations in chlorine prices.

Electricity costs are typically over half of total manufacturing costs for chlor–alkali producers, whereas feedstock costs are usually less than 15%. Potentially, the lowest industrial electricity costs, within the EU, are found in the Netherlands and the UK. This is due to gas industry and electricity deregulation. The UK chlor–alkali industry is therefore expected to be competitive within European markets.

A major debate within the chlor–alkali industry worldwide concerns the possible replacement of mercury electrolytic cells by membrane or diaphragm cells for environmental reasons. Europe has the largest number of mercury cells worldwide. There is a Paris Convention recommendation to phase out use of mercury cells by 2010. In practice, projects to replace mercury cells in Europe have been very infrequent over the last 15–20 years. Much of the chlor–alkali industry argues that the environmental benefit gain is too small for the large capital cost entailed (eg over £200 million).

Other chlorine-related markets

Chlorine and ethylene are used to make VCM (vinyl chloride monomer) which is converted into PVC and is the largest end-use for chlorine. Most increases in chlorine production worldwide are likely to be related to increased VCM/PVC production.

Hydrochloric acid markets in Europe usually tend to be in oversupply. This is due to large volumes of acid made as a by-product in the production of PVC plastic.

Aluminium chloride is mainly used as a catalyst in the petrochemical industry and this is a mature market. Although a speciality chemical, production and sales are unlikely to change to a significant extent.

Ferric chloride is a mature chemical product mainly used in the water treatment industry. The chemical is usually produced as a by-product or when steels are pickled with hydrochloric acid. Total European production is estimated at about 100 ktpa.

Phosgene is widely used in the UK chemical industry, despite its highly toxic nature. It is classified as a growth product because both polyurethane and polycarbonate plastics are high-growth chemicals. In future, the cost of chlorine will probably determine the economics of phosgene production.

Sodium hypochlorite (bleach) is commonly produced as a by-product from chlorine manufacture. However, many of its pulp-bleaching and other industrial uses have been superseded by chlorine dioxide, so sodium hypochlorite is viewed as a mature chemical product.

Lithium metal is a growth product due to its use in batteries.

Siloxane is a type of plastic based on silicon rather than hydrocarbons. Methyl chloride is a major feedstock in the manufacture of siloxane, which is a high-growth product in the UK.

(b) Reported prices

Chlorine price trends have fluctuated over the last three years at around $200 per ton. Producers of the whole chlorine/VCM/PVC chemical chain enjoyed high prices in 1995. However, absolute chlorine prices are high by historical standards. For instance, during the previous decade average prices were closer to $100 per ton.

(c) Financial results

Recent financial results for a typical chlorine-based inorganic chemical company are shown in Figure 5.4. Typical return on capital has increased in recent years. In 1994 one company said that its chlor–alkali business will be able to generate 20% return on net assets.

A current return on investment for a typical chlorine plant (of about 180 ktpa capacity based on the membrane process) is estimated to be 16%, which is acceptable. However, chlorine prices are currently high on an historical basis and the co-product caustic soda price has a marked effect on the economics of the brine electrolysis process.

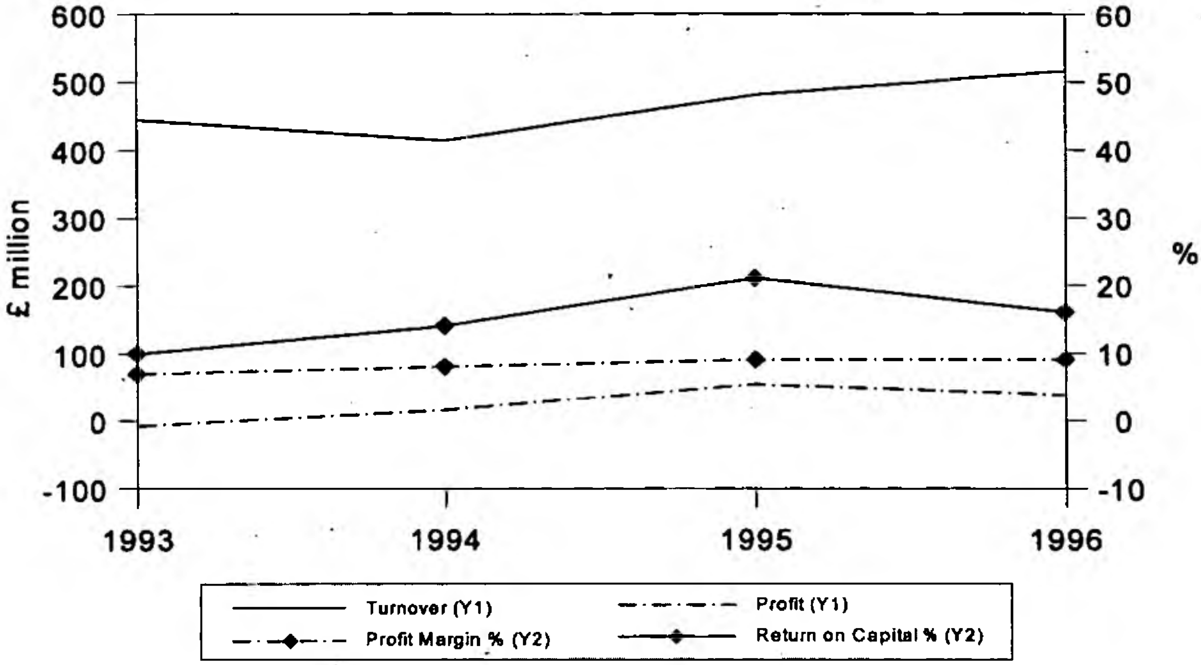
Return on investment for a new hydrogen chloride plant (20 ktpa capacity, anhydrous) is estimated at 18% (showing an acceptable ROI). It is more difficult to estimate an ROI for the phosgene production process, as reported prices of nearly £1000 per ton are based on 1 ton cylinders. It is probable that bulk prices for phosgene would be significantly lower than these prices reported for 1 ton cylinders. Owing to its toxic nature, bulk production tends to be made in situ for direct use in downstream plant. Economics are therefore linked directly to the downstream market.

A typical company producing chlorine would be larger than the average chemical company in the UK and would have an above-average credit rating for UK industry as a whole. The financial strength of a typical company in other chlorine-related sectors is not as strong, but is still above average for UK industry.

(d) Economic outlook

Chlorine has one major end-use, the manufacture of PVC plastic, and many small-volume applications within industry. The likely outlook for PVC is that Western European and UK

Figure 5.4 *Inorganic chlorine-related manufacturers – typical financial results*



demand will remain steady and exports are unlikely to grow. A continuing deterioration in PVC prices from the peak in 1995 through to the bottom of the petrochemical cycle, due 1999–2000, can be expected. However, as half the feedstock is another petrochemical (ethylene), which is also likely to fall in price, the profitability of PVC production will be partly protected. The UK remains a good location for VCM/PVC production for the European market because both electricity and ethylene can be comparatively competitively priced in the UK.

Many of the smaller uses for chlorine have already declined under environmental pressure, eg chlorine for pulp and paper bleaching, hypochlorite bleaches, chlorine in water treatment and, of course, chlorine for organic CFCs. However, smaller uses for chlorine within the chemical industry are likely to show above-average growth, eg for titanium dioxide, phosgene, propylene oxide, pharmaceuticals and organic chlorides.

A major use for co-product caustic soda is in the production of aluminium from alumina ore. Future growth in light–weight metal production will support growth in chlor–alkali production. However, any crisis in this industry will adversely impact chlor-alkali. Sentiment within the aluminium industry is reflected in Australian alumina three-year contracts.

Given the 'unusually' high price of chlorine in recent years and the cyclic nature of the industry, it is to be expected that chlorine price will trend downwards in the medium-term future while caustic soda prices move up. This will leave the economic position of chlorine producers unchanged but should benefit the economics of chlorine-consuming industries.

5.2.5 Inorganic bromine/fluorine/iodine related Industries

(a) Market overview

Of all the halogen group of chemicals, chlorine is the only large-volume industry. For the three other halogens – bromine, fluorine and iodine – each industry is small volume and highly specialised with generally no more than two medium-sized manufacturers in each sector in the UK.

Bromine

Bromine is produced from sea water in the UK using chlorine as a feedstock in the process. It is the largest such operation in Europe. Liquid bromine is a speciality chemical used as a pharmaceutical intermediate and for agrochemicals. A large proportion of the production is also used to make ethylene dibromide. This is used as a scavenger for lead used in petrol. This use will decline with the EU decision to ban leaded gasoline in year 2000.

Fluorine

One company is a major producer of inorganic fluorides. Commercial-grade hydrofluoric acid is produced near Sheffield for the stainless steel pickling industry and for use in crystal glass manufacture. The company also produces very high-purity fluorine chemicals for the semiconductor/electronics industry. In 1995 there was a plan to build a UK plant to produce 3 ktpa high-purity HF acid based upon continuing growth in demand for ultrahigh- purity chemicals.

The company is also the world's largest producer of potassium fluoroborate and potassium fluorotitanate used for aluminium (grain) refining.

Potassium fluoride

Potassium fluoride is a speciality chemical with a wide range of applications notably for the production of agrochemicals as an intermediate for root-crop pesticides.

Potassium iodide

Potassium iodide has a wide range of small-volume uses and is a speciality chemical.

(b) Reported prices

The price of chemicals made from fluorine have increased within the last three years. Also consumers of iodine have had to pay higher prices for their feedstock.

(c) Financial results

Recent financial results for bromine-, fluorine- and iodine-based inorganic chemical companies are shown in Figure 5.5. A typical company appears to have been profitable in the last two years.

One company claims that it looks for high margins and a high (20%) return on investment for all of its products.

A typical medium-sized company in this sector would be larger than the average chemical company in the UK and would have a credit rating of above average for the UK industry as a whole. However, the credit rating for some of the smaller companies is not so strong.

(d) Economic outlook

Despite the speciality nature of the chemicals produced by this subsector, any high prices achieved do not appear to be reflected in the financial results of a typical company.

5.2.6 Titanium dioxide industry

(a) Market overview

Titanium dioxide is a widely used pigment, with demand closely linked to growth in housing, the automobile and the coatings industries. It is a typical commodity product with major product price and profitability cycles. The cycles are not expected to be always in phase with the overall chemicals industry cycle. In the last cycle, good profitability in mid/late 1980s led to major new-plant investment, which resulted in overcapacity, poor markets and lower profitability in the recession of the early 1990s. By 1994 titanium dioxide markets started to improve, only to deteriorate in 1995 and again in early 1997. In 1997 major new capacity projects in the US were delayed and now the industry profitability is reportedly improving.

Since 1994 in Europe most investment has been for de-bottle necking projects where companies have introduced new process technology, catalysts, etc, to boost output at existing facilities.

On a worldwide basis, the sulphate process has dropped from 65% of total capacity in 1985 to 45% in 1993 and is forecast to account for 35–40% by 2000. It is likely that there will be a residual market for the sulphate-based TiO_2, where there is still demand for the anatase pigment. For sulphate producers, the markets for by-product materials (eg ferric sulphate and gypsum) are economically important.

(b) Reported prices

Titanium dioxide prices improved in 1996, languished in early 1997 and recovered after expansion plans were delayed. Recent

Figure 5.5 ***Inorganic bromine/fluorine/iodine-related manufacturers – typical financial results***

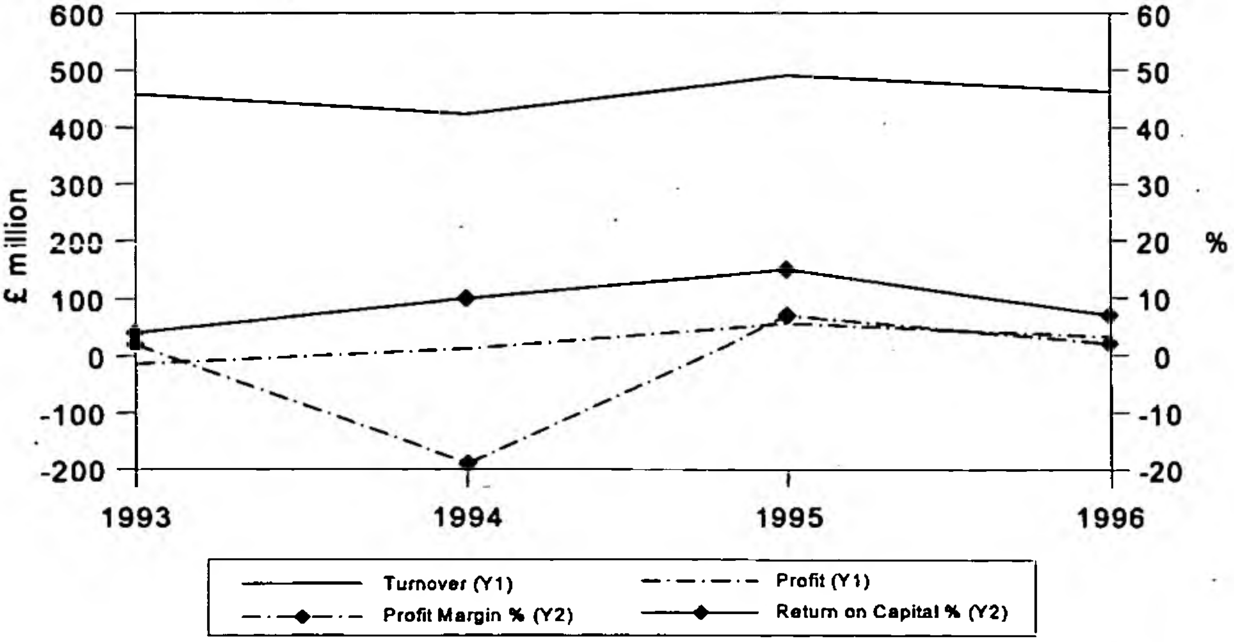
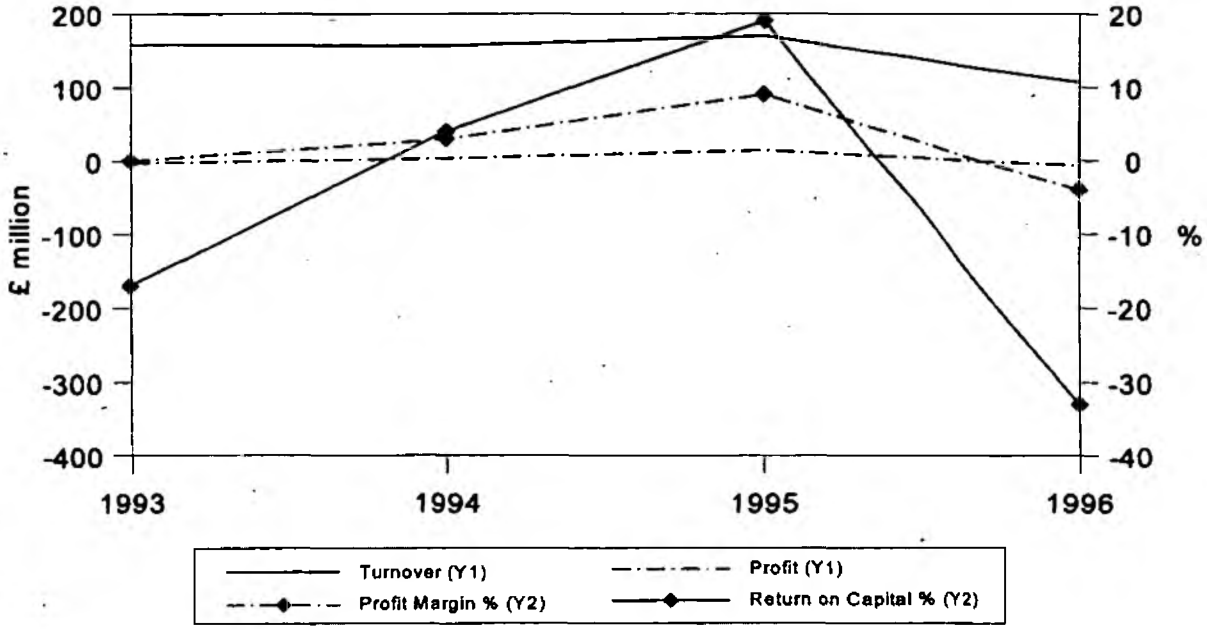


Figure 5.6 ***Inorganic titanium dioxide-related manufacturers – typical financial results***



titanium dioxide prices have tended to be higher on a historical basis with values close to $1 per lb.

(c) Financial results

Recent financial results for a typical titanium dioxide company are shown in Figure 5.6.

The decline in return on capital in 1996 relates to one result and is probably unrepresentative of the long term economic performance of the sector.

Current returns on investment for typical titanium dioxide plants (100 ktpa capacity), are estimated to be 31% for the chloride route and 24 % for the sulphate route. The sulphate route appears to be profitable, particularly when using a relatively high titanium dioxide feed. The chloride process appears overall to be the more economic route, due to lower capital costs.

A typical company in the titanium dioxide sector would be larger than the average chemical company in the UK and would have a credit rating of above average for UK industry as a whole.

(d) Economic outlook

It is likely that the titanium dioxide industry will continue to operate at 95% of capacity or better throughout 1998 and that product prices will trend upwards according to stock market analysts. This can only improve the short term economics of the UK's titanium dioxide production industry.

Recently, both UK producers have announced plans for medium size (£30 – £70 million) investments to expand capacity of UK chloride-based production.

5.3 Cost of abatement

5.3.1 Abatement of sulphuric acid plant

Costs of abatement of sulphuric acid plants have been developed in terms of SO_2 recovered per tonne of daily installed capacity of sulphuric acid. The baseline used is the single absorption process, without abatement. The approximate incremental cost for each abatement process, applied to the baseline plant, is summarised in Table 5.1.

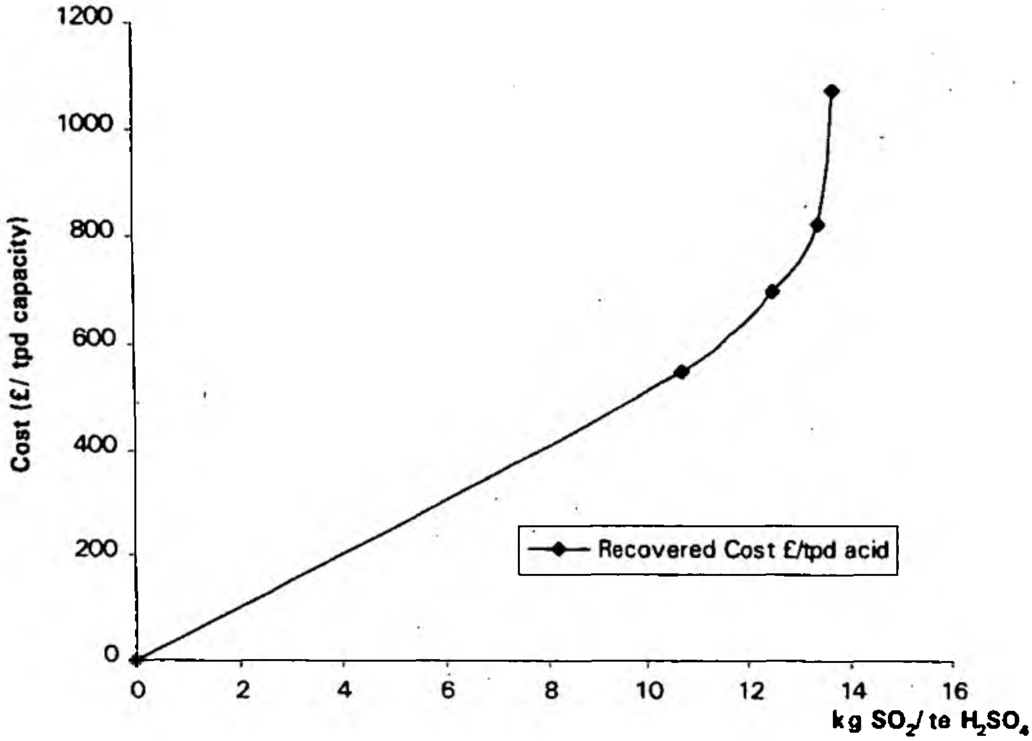
The basis for Table 5.1 is as follows:

- SO_2 concentration at the inlet to the converter is 10 vol %.
- Cost data have been developed for a 1000 tpd sulphuric acid plant.
- Processes considered for abatement are conversion to double absorption (DA), introduction of additional catalyst beds (five-bed), use of "low bite" catalyst to improve conversion and finally addition of a secondary abatement system for the tail gas.

Table 5.1 ***Annualised cost of abatement for sulphuric acid plant***

Process	Conv'n (%)	kg SO_2/t acid	Cost (£/tpd acid)
Single absorption	98	14	0
Double absorption	99.5	3.3	498
Five-bed DA	99.8	1.5	698
Five-bed DA + low bite	99.9	0.6	822
Extra abatement	99.95	0.3	1070

Figure 5.7 *SO_2 Abatement costs per tonne recovered*



These results are expressed graphically in Figure 5.7 in terms of *additional* SO_2 recovery compared with the single absorption process. The graph essentially shows an exponential increase in cost as recovery efficiencies approach 100%.

The extra abatement system included in Table 5.1 is the peroxide-based process. Hydrogen peroxide should achieve efficient recovery of SO_2 at a relatively low capital cost. It is however an expensive chemical and will result in higher operating costs. Alternative abatement processes such as activated carbon, or lower-priced solvents in absorption systems will reduce operating costs, at the expense of further increases in capital cost.

The information illustrates that extra gains in conversion efficiency or abatement are approaching the limits of reasonable cost above 99.8 – 99.9% overall conversion.

Insofar as the techniques discussed above are commercially available currently, the combination of double absorption with improved catalyst performance and a further stage of tail gas abatement should be considered BAT.

Table 5.1 costs apply to new-plant abatement. The use of some of the same abatement techniques may be feasible for many existing plants, currently having lesser degrees of abatement. It is likely, however, that costs would be expected to be higher for the abatement of existing plant.

The cost data are approximate and indicative of cost trends. It should also be noted that overall plant efficiency is related to inlet concentration of SO_2 to the converter. As a result, the values estimated above are only appropriate for the 10% SO_2 case used. The costs will vary considerably with plant design, capacity and operating conditions, and should be derived for specified conditions, when assessing BAT vs BATNEEC requirements.

5.3.2 Abatement of nitric acid plant

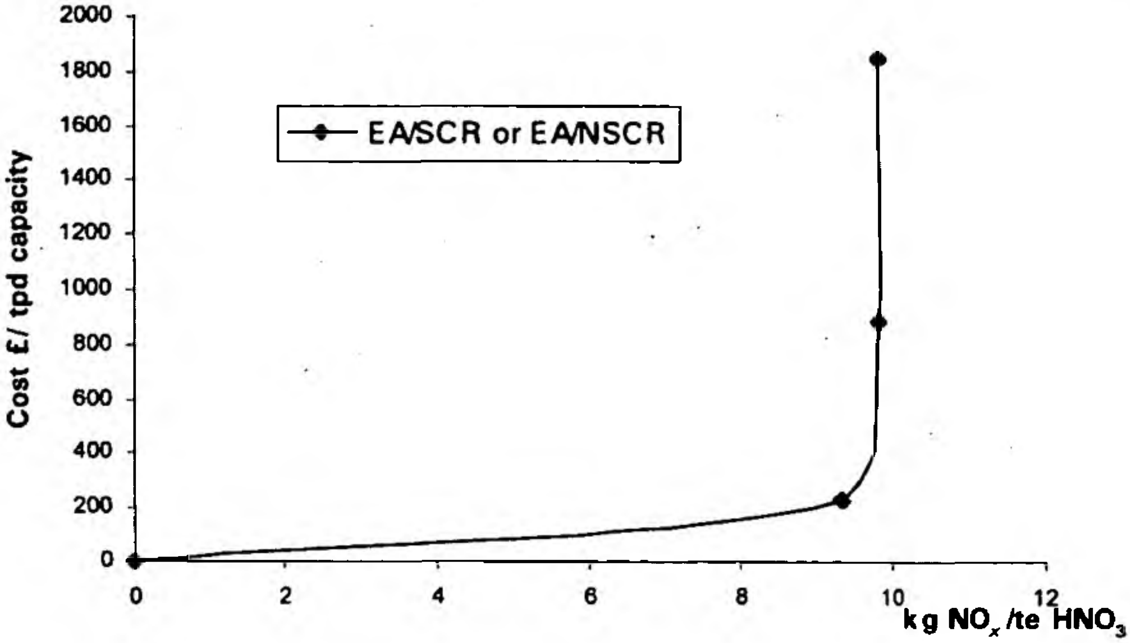
Costs of abatement of nitric acid plants are provided and are expressed in terms of NO_2 recovered per tonne of daily installed capacity of nitric acid. The three most common abatement methods have been considered. These are extended absorption (EA), EA in combination with selective catalytic reduction (SCR), and EA in combination with non-selective catalytic reduction (NSCR).

The cost data for each type of abatement method are based on a range of nitric acid plants, including various low, medium and high dual pressure plant designs. The data should therefore be regarded as indicative only. The baseline is the non-abated dual pressure plant. The incremental cost for each abatement process is summarised in Table 5.2 for a new 1000 tpd nitric acid plant. Additional costs of using the same techniques of abatement for existing plant are likely to be greater, depending on the particular circumstances of the facility.

Table 5.2 *Annualised cost of abatement for nitric acid plant*

Abatement method	kg NO_2/t acid	Cost (£/tpd acid)
None	9.7	0
EA	0.5	230
EA + SCR	0.15	880
EA + NSCR	0.12	1850

Figure 5.8 ***NO_x abatement costs per tonne NO_x recovered***



The results are expressed graphically in Figure 5.8 in terms of additional NO_2 recovery compared with the non-abated process. The graph shows essentially an exponential increase in cost as recovery efficiencies approach 100%.

The information illustrates that extra gains in conversion efficiency or abatement are approaching the limits of reasonable cost above 99.8–99.9% overall conversion.

Insofar as the techniques discussed above are commercially available currently, the combination of extended absorption with either SCR or NSCR should be considered BAT for NO_x releases. The abatement of nitrous oxide (N_2O), however, with respect to its ozone depletion potential and 'greenhouse effect', is favoured by a combination of extended absorption and NSCR.

The cost data should therefore be used cautiously and be considered only as indicative of cost trends. The costs will vary considerably with plant design, capacity and operating conditions and should be derived for specified conditions.

5.3.3 Abatement of halogen plants

The specific concerns of chlorine production relate to diaphragm and mercury cells. The former uses asbestos to separate anolyte and catholyte, whilst the latter uses mercury as the cathode. BPEO would probably involve new plants being constructed using membrane cells, which do not create 'additional' environmental concerns, above those normally generated in producing chlorine. This approach is also in line with the PARCOM Recommendation (15) to phase out mercury-based processes.

(a) Diaphragm Cells

BAT for asbestos requires compliance with the Asbestos Regulations in terms of safe handling and disposal of spent diaphragms.

(b) Mercury Cells

BAT for mercury cells requires removal of mercury contamination from all product streams and all emission sources to achieve very low release levels. BAT, therefore, requires the application of a combinations of techniques, including:

- chilling and use of activated carbon to remove mercury from hydrogen;
- mechanical/ physical recovery of Hg downstream of the cells;
- demercurisation of caustic soda or potash with activated carbon-coated plate or candle filters;
- use of oxidants to treat process gases;
- demercurisation of liquid effluents by precipitation to HgS; and
- redesign of cells to minimise mercury content and contact.

Costs for these abatement techniques are generally developed for specific plant. It is therefore not possible to present these in a way that provides trends. However, as an illustration the capital required to reduce mercury in the strong and weak hydrogen streams to less than 0.01 mg/m^3 would be about £30 to £40 per installed tonne of chlorine capacity for a small chlorine plant.

Abating releases from halogen processes, other than in respect of mercury removal or asbestos handling, should be considered in terms of treating the gaseous and liquid streams to minimise emissions and render them harmless. BAT techniques for halogens, halides and caustic liquors are well established and are discussed in Section 2.4 "Halogens" and Section 3 "Best available techniques for controlling releases".

5.3.4 Abatement of titanium dioxide plant

(a) Sulphate Process

The sulphate process produces large quantities of waste material including metallic sulphates. BAT represents the conversion of these materials into useful saleable by-products, leading to minimisation of the releases to the environment. BAT processes for the sulphate route include:

- conversion of ferrous sulphate to ferric sulphate (a water treatment chemical);
- conversion of spent acid to white or red gypsum (for wall boarding and agricultural land improvement, respectively); and
- recycle of dilute acid produced by removal of SO_2 from calciner off-gases.

The sulphate process also produces weak acid, SO_x, NO_x and particulates. Provision of BAT is in accordance with recognised techniques that are described in Sections 2.2; 2.3 and 5 of this Guidance Note and include:

- abatement for SO_x , NO_x and particulates, arising from fuel firing and calcining, and alternatives such as
- removal of particulates from waste gases;
- subsequent recovery of the SO_2 generated by roasting of metal sulphates to make sulphuric acid via the contact process;
- recycling the metal oxides produced by roasting to the steel industry; and
- concentration or regeneration of the spent sulphuric acid for recycle or sale.

(b) Chloride process

Tail gases from the chlorination stage of the process contains carbon monoxide, carbon dioxide with some hydrogen chloride and chlorine 'slip' from the reaction. Conventional two-stage scrubbing techniques, first with demineralised water to remove the hydrogen chloride and then caustic to remove chlorine, represent BAT. All other vents are scrubbed with caustic to remove chlorine and make hypochlorite.

BAT for the carbon monoxide generated by oxidation of the coke bed of the chlorinator requires the thermal conversion of the monoxide in the tail gas to carbon dioxide.

It is also practicable to convert the metallic chlorides in the waste material to the more inert oxide form, which will have a reduced environmental impact and may have value as a by-product. Inclusion of this conversion step also represents BAT for the chloride process.

5.3.5 Abatement of particulate matter

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 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 that 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 5.3. 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 for various particulate sizes***

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

When selecting particulate abatement systems other considerations 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 considered under this sector, but approximate costs of employing some of the particulate abatement control techniques discussed in this Guidance Note are given in Figures 5.9 and 5.10. They should be treated with considerable caution as they will vary greatly for specific applications. The data show total installed equipment costs and annualised costs against volumetric throughput for each of the main technologies.

Figure 5.9 ***Installed capital cost for particulate abatement equipment***

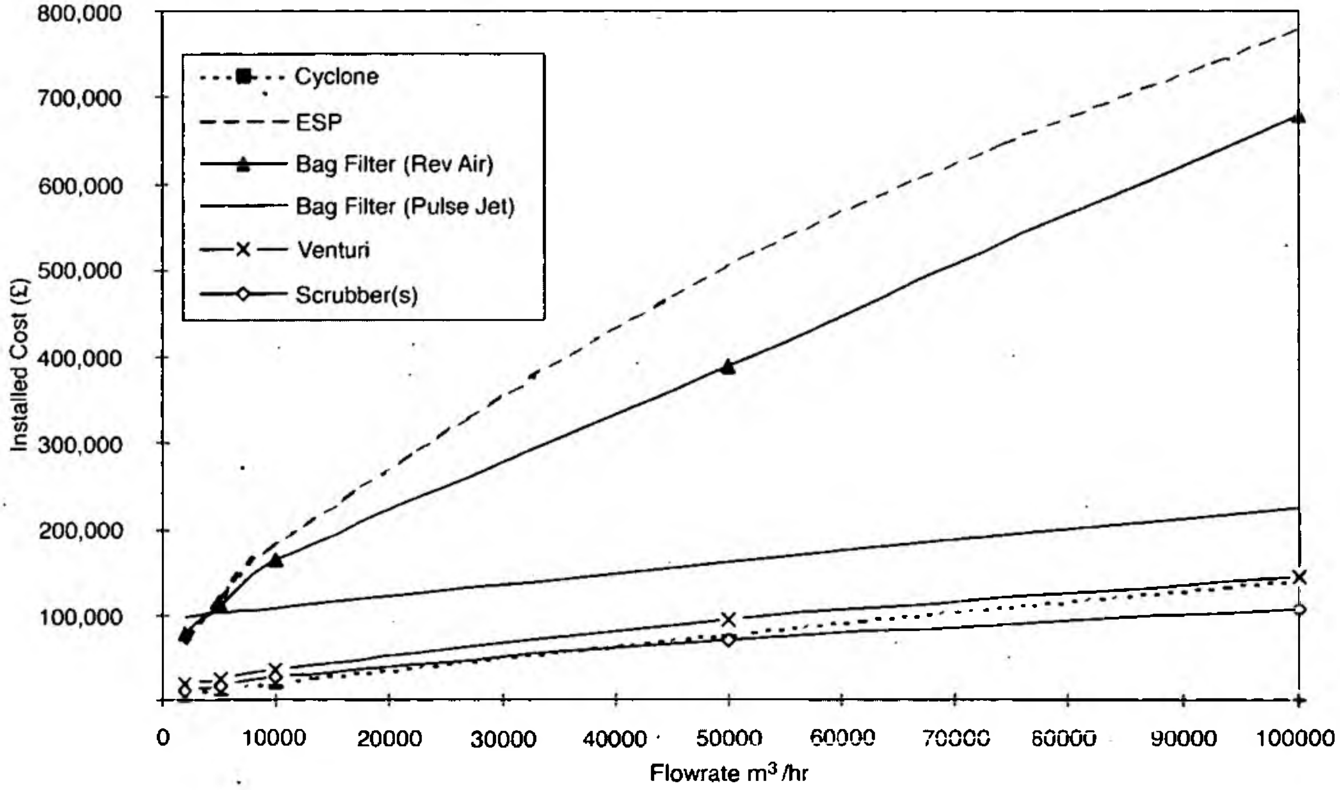
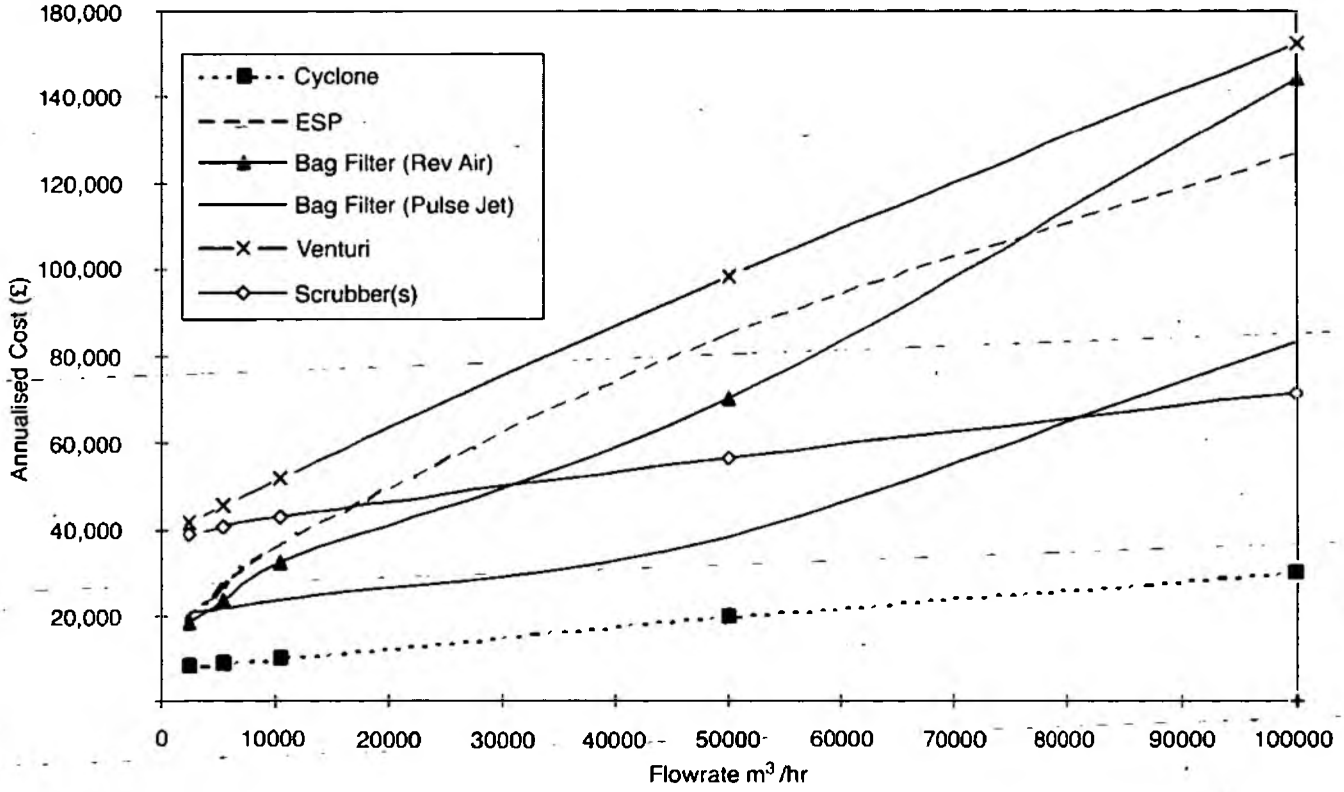


Figure 5.10 ***Total annualised costs for particulate abatement equipment***

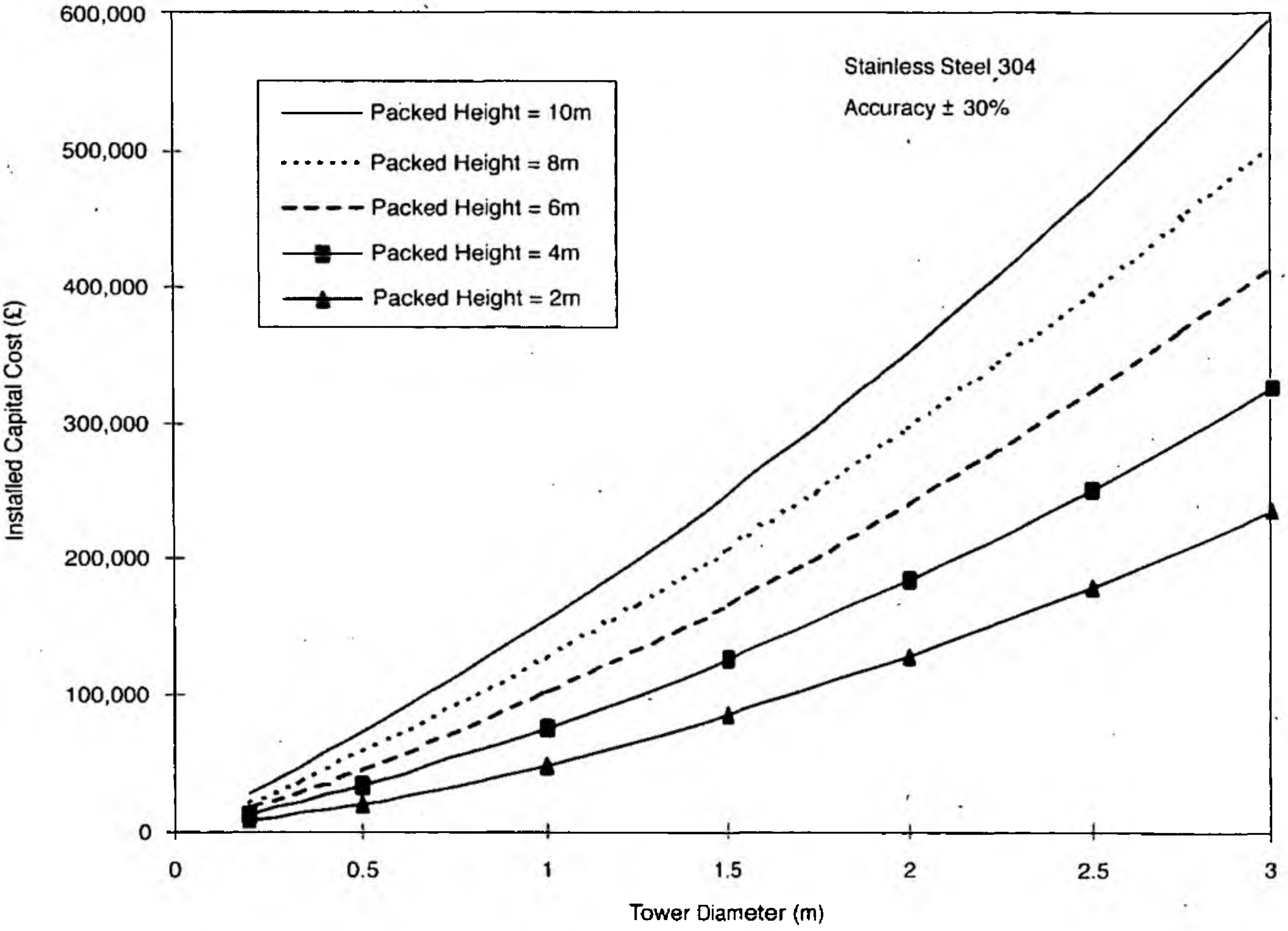


5.3.6 Abatement by gas scrubbing

Scrubbing techniques are widely used in this sector. Some are fully integrated into the process and operate at elevated temperatures and pressures and their costs are very specific to the process.

Even for more general-purpose scrubbers, the diverse nature of the pollutants, the scrubbing medium and operating conditions make it impracticable to give average annualised costs. Figure 5.11 shows capital costs only for a common type of scrubbing equipment constructed in stainless steel.

Figure 5.11 ***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* in 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 IPC 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)).

Inspectors should refer 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 text 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 conducted by a recognised method and reported.

Where appropriate, continuous monitoring techniques should be used. However, Inspectors should be aware of the limitations and accuracy of continuous monitors. Regular calibration checks should be carried out and documented. When continuous monitoring is not appropriate or available, non-continuous monitoring should be undertaken, together with continuous surrogate measurements where applicable.

In requiring the use of continuous monitoring for any given release point, Inspectors should take into account factors such as 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.

All final releases to air should be essentially colourless, free from persistent trailing mist or fume and free from droplets.

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;
- BOD;
- hydrocarbon oil;
- ammoniacal and total nitrogen;
- suspended solids;
- phenols;
- sulphides;
- 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(38), 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)(39) 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(40), the Montreal Protocol(38) 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 its vapour pressure, 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(5) 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^3 for continuous releases. Her Majesty's Inspectorate of Pollution, now the Environment Agency, published two Technical Guidance Notes(3), (4) on pollution abatement technology that 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^3 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^3.

  For mixed streams the release level may be calculated by summing the class levels 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 substances or for TOC.

  HMIP Technical Guidance Note M2(5) 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 the relevant IPCGN S2 5.01 (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

1 *The Environmental Protection (Prescribed Processes and Substances) Regulations 1991.* SI 472. ISBN 0-11-013472-9; as amended by:

The Environmental Protection (Amendment of Regulations) Regulations 1991. SI No 836, ISBN 0-11-013836-8

The Environmental Protection (Prescribed Processes and Substance) (Amendment) Regulations 1992. SI No 614, ISBN 0-11-023614-9

The Environmental Protection (Prescribed Processes and Substances) (Amendment) Regulations 1993. SI No 1749, ISBN 0-11-034749-8

The Environmental Protection (Prescribed Processes and Substances) (Amendment) (No 2) Regulations 1993. SI No 2405, ISBN 0-11-035405-2

The Environmental Protection (Prescribed Processes and Substances, etc) (Amendment) Regulations 1995. SI 1995 No 3247, ISBN 0-11-053799-8

The Environmental Protection (Prescribed Processes and Substances, etc) (Amendment) (Hazardous Waste Incineration) Regulations 1998. SI 1998 No 767, ISBN 0-11-065758-6

2 *Integrated Pollution Control: A Practical Guide.* Department of the Environment/Welsh Office, (TSO), ISBN 0-11-752750-5

Guidance Notes to Applicants for Authorisation – processes prescribed for regulation by the Environment Agency, available from the Agency

3 *Monitoring Emissions of Pollutants at Source.* HMIP Technical Guidance Note (Monitoring) M2. (TSO) January 1994, ISBN 0-11-752922-2

4 *Guidelines on Discharge Stack Heights for Polluting Emissions.* HMIP Technical Guidance Note (Dispersion) D1. (TSO) June 1993, ISBN 0-11-752794-7

5 *Environmental, Economic and BPEO Assessment Principles for Integrated Pollution Control.* HMIP Technical Guidance Note (Environmental) E1

6 *Released Substances and their Dispersion in the Environment.* Environmental Analysis Cooperative. (TSO) 1996. ISBN 0-11-702010-9

7 *EC Directive on the Combatting of Air Pollution from Industrial Plants* (framework). 84/360/EEC, (OJ L188, 16/7/84)

8 IPCGN S2 4.04 *Inorganic Chemicals.* (TSO) 1999, ISBN 0-11-310140-6

9 *The Air Quality Standards Regulations 1989.* SI No 317, ISBN 0-11-096317-2

10 *The Air Quality Regulations 1997.* SI No 3043, ISBN 0-11-065315-7

11 *The Surface Waters (Dangerous Substances Classification) Regulations 1989.* SI 1989, No 2286

12 *Protocol to the 1979 Convention on Long Range Transboundary Air Pollution on Further Reduction of Sulphur Emissions.* Oslo 1994

13 *Reducing Emissions of Volatile Organic Compounds (VOCs) and Levels of Ground Level Ozone: A UK Strategy.* DETR, Ashdown House, 123 Victoria Street, London SW1E 6DE

14 *EC Directive relating to 1,2- dichloroethane, trichloroethylene, perchloroethylene and trichlorobenzene.* 90/415/EEC

15 *PARCOM Decision 90/3 concerning the Reduction of Atmospheric Emissions from Chlor–Alkali Plants.*

16 *EC Directive on Mercury Releases from Chlor–Alkali Plants to Water* 82/176/EEC

17 *EC Directive on Procedures for Harmonising the Programmes for the Reduction and Eventual Elimination of Pollution caused by Waste from the Titanium Dioxide Industry.* 92/112/EEC

18 *Policy and Practice for the Protection of Groundwater.* 2nd edition. Environment Agency. (TSO) 1998, ISBN 0-11-310145-7

19 *EC Directive on the Protection of Groundwater against Pollution caused by Certain Dangerous Substances.* 80/68/EEC

20 IPCGN S2 4.01: *Large-Volume Organic Chemicals.* (TSO) 1999, ISBN 0-11-310153-8

21 IPCGN S2 4.02: *Speciality Organic Chemicals.* (TSO) 1999, ISBN 0-11-310154-6

22 IPCGN S2 3.02 *Asbestos Processes.* (HMSO) 1996, ISBN 0-11-310118-X

23 Air Pollution Advisory and Review Group, Air Quality Division, DETR, Ashdown House, 123 Victoria Street, London SW1E 6DE

24 The Environmental Technology Best Practice Programme, ETSU, Harwell, Oxfordshire OX11 0RA
Help line 0800 585794
Good Practice Guides (relevant selection):

GG12 Solvent Capture for Recovery and Re-Use from Solvent-Laden Gas Streams

GG71 *Cost-Effective Reduction of Fugitive Solvent Emissions*

GG37 *Cost-Effective Separation Technologies for Minimising Wastes and Effluents*

GG54 *Cost-Effective Membrane Technologies for Minimising Wastes and Effluents*

25 *Waste Minimisation Guide.* Institution of Chemical Engineers. Prof B. D. Crittenden, Dr S. T. Kolaczkowski. February 1992

Waste Minimisation – An Environmental Good Practice Guide for Industry. Environment Agency, 1998

US Environmental Protection Agency (1988). *Waste Minimisation Opportunity Assessment Manual*, US EPA Hazardous Waste Engineering Research Laboratory, Ohio

26 *Best Available Techniques for the Control of Pollution in Acid and Halogen Processes.* Research Report No P.200. Environment Agency, 1998

27 International Standards Organization (ISO), *Standard for Environmental Management Systems,* ISO 14001

Regulation (1836/93) allowing voluntary participation by companies in the industrial sector in a Community eco-management and audit scheme (EMAS). Official Journal L168/1, 10/7/93

28 *Responsible Care*, Chemical Industries Association, London

29 *Combustion Processes: Large Boilers and Furnaces 50 MW(th) and Over.* Chief Inspector's Guidance Note S2 1.01. (HMSO) November 1995, ISBN 0-11-753206-1

30 *Waste Incineration.* IPC Guidance Note S2 5.01. (TSO) October 1996, ISBN 0-11-310117-1

31 *Pollution Abatement Technology for Particulate and Trace Gas Removal.* HMIP Technical Guidance Note (Abatement) A3. (TSO) April 1993, ISBN 0-11-752983-4

32 *Pollution Prevention Guidelines: Above Ground Oil Storage Tanks.* PPG2. Environment Agency and Scottish Environmental Protection Agency

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33 Pollution Prevention Guidelines, PPG3. *Use and Design of Oil Separators in Surface Water Drainage Systems.* Environment Agency

34 *BS 5908: 1990 Code of practice for fire precautions in the chemical and allied industries*

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Waste Management, The Duty of Care, A Code of Practice. HMSO, ISBN 0-11-752557-X

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38 *Montreal Protocol on Substances that Deplete the Ozone Layer.* CM283. (TSO) ISBN 0-10- 102832-6

39 *Categorisation of Volatile Organic Compounds.* DOE 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

40 *The Chemicals (Hazard Information and Packaging) Regulations Approved Supply List.* (TSO) ISBN 0-11-882156-3

41 *Pollution Abatement Technology for the Reduction of Solvent Vapour Emissions* HMIP Technical Guidance Note (Abatement) A2. (TSO) March 1994, ISBN 0-11-752925-7

Abbreviations and definitions of terms used

BAT	Best Available Techniques
BATNEEC	Best Available Techniques Not Entailing Excessive Cost
BPEO	Best Practicable Environmental Option
BOD	Biological oxygen demand
CFCs	Chlorofluorocarbons
CIGN	Chief Inspector's Guidance Note
CO	Carbon monoxide
CO_2	Carbon dioxide
COD	Chemical oxygen demand
DCE	Dichloroethane
DETR	Department of the Environment, Transport and the Regions
EP	Electrostatic precipitator
EPA90	The Environmental Protection Act 1990
ETBPP	Environmental Technology Best Practice Programme
ETP	Effluent treatment plant
g/h	grams per hour
HCFCs	Hydrochlorofluorocarbons
HEPA	High-efficiency particulate arrestment
HMIP	Her Majesty's Inspectorate of Pollution
HNO_3	Nitric acid
H_2O_2	Hydrogen peroxide
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
HSE	Health and Safety Executive
IPC	Integrated Pollution Control
IPCGN	IPC Guidance Note
kg/h	Kilograms per hour
ktpa	Kilotonnes per annum
mg/m^3	Milligrams per cubic metre
NH_3	Ammonia
Nm^3	Normal cubic metre
NO	Nitric oxide
N_2O	Nitrous oxide
NO_2	Nitrogen dioxide
NO_x	Oxides of nitrogen, may be NO, NO_2
OSPARCOM	Oslo/Paris Conventions for the Prevention of Marine Pollution
PARCOM	Paris Convention
PVC	Poly (vinyl chloride)
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
TGN	Technical Guidance Note
TiO_2	Titanium dioxide
TOC	Total organic carbon
TSO	The Stationery Office
tpd	Tonnes per day
VCM	Vinyl chloride monomer
VOC	Volatile organic compound

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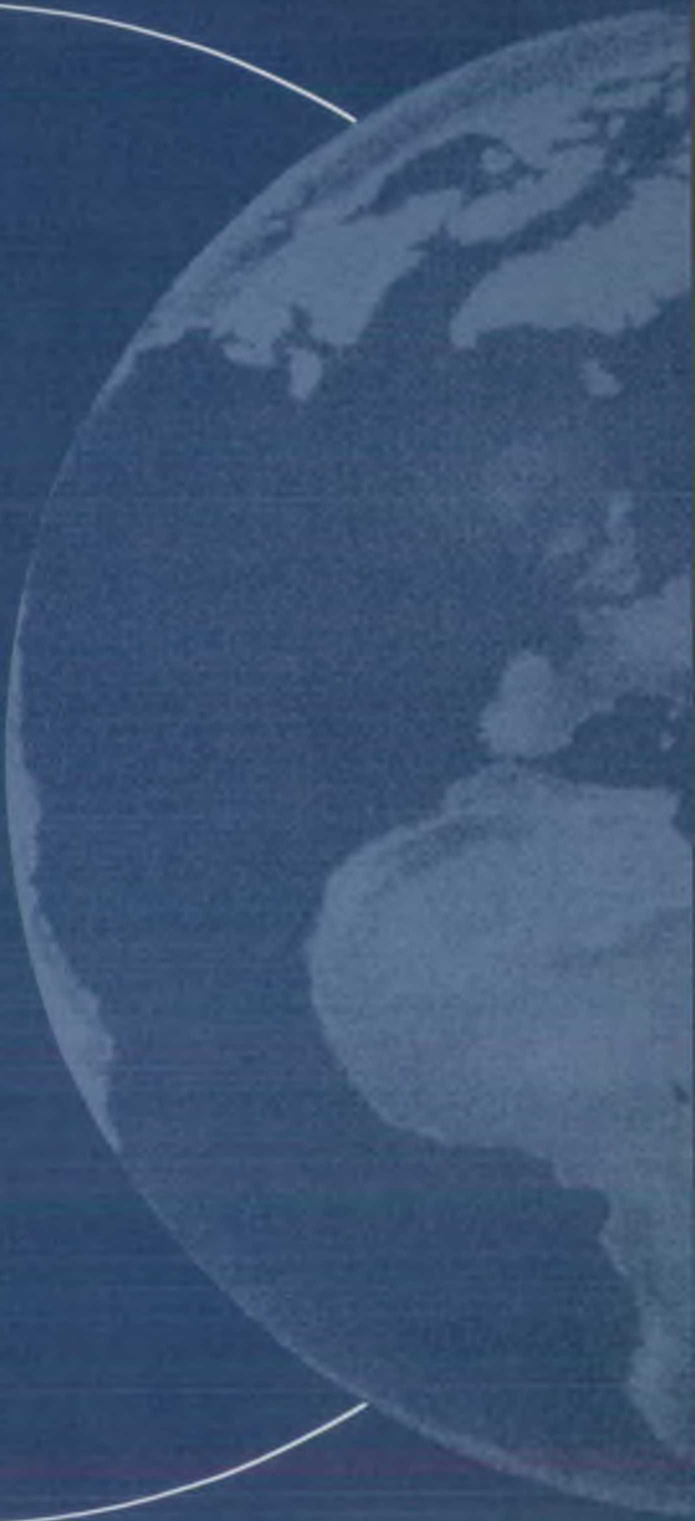

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