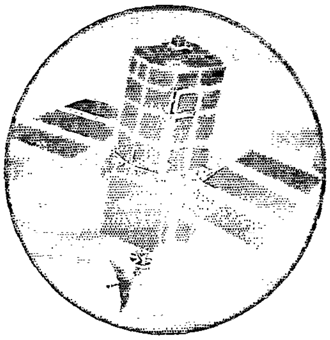
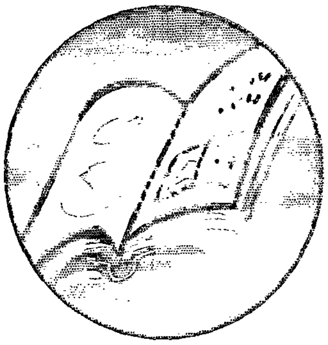
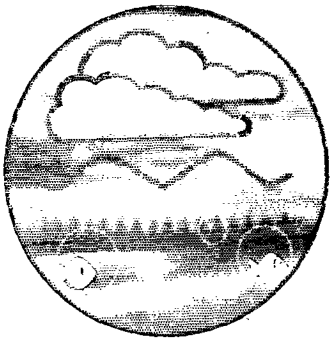
Best Available Techniques for Inorganic Acid and Halogen Processes







Research and Development

Technical Report
P200

ENVIRONMENT AGENCY

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Best Available Technique for Inorganic Acid and Halogen Processes

Technical Report P200

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Statement of use

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

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EXECUTIVE SUMMARY

This report has been prepared by Foster Wheeler on behalf of the Environment Agency to provide information on inorganic acid and halogen production processes. The report will provide background material for use in the revision of the Chief Inspector's Guidance Notes to Inspectors. The processes, which are covered in existing guidance notes and assessed in this report are:

Sulphuric Acid Production (Chief Inspectors' Guidance Note IPR 4/10)
Nitric Acid Production (IPR 4/11)
Halogens, Halides and Oxyhalogens Production (IPR 4/13 and 4/14)

The two routes to titanium dioxide production are currently dealt with separately in existing Guidance Notes 4/10 (Sulphate Route) and 4/13 (Chloride Route). In this report both titanium dioxide production routes are discussed in their own section, independently of other processes.

The main objectives of this report, in respect of the above processes, are to assimilate worldwide information and to provide an overview of the extent of the differences in best available techniques (including process selection and pollution abatement) between the UK and other leading industrialised environmentally advanced countries. The information will be used to support the development of a consolidated Guidance Note, that covers the above processes.

The processes dealt with by this report are centred on industry sectors which operate mature technologies. No major developments appear to have occurred in process/production selection in the last five years and older processes operate side by side with newer investment, usually of similar or improved process technology.

Overall reduction in polluting releases has generally occurred through the improved application of existing abatement techniques. However some process developments and improvements in abatement technology have occurred since the publication of the existing Chief Inspector's Guidelines in 1993. Examples of these changes, which are described more fully in the relevant sections of this report, are:

- Use of activated carbon for recovery of sulphuric acid from SO_2 tail gas (in the development stage). This will be a yield enhancer if fully developed.
- Use of an amine regenerative process to produce SO_2 (also in the development stage).
- Improvements in the performance and cost effectiveness of the selective catalytic reduction (SCR) process for NO_x abatement.
- The effectiveness of non selective catalytic reduction (NSCR) to abate nitrous oxide (N_2O) as well as NOx.
- Use of zirconium catalysts in the high-pressure absorption nitric acid process (development stage). This is reported to achieve low levels of NO_x emission without the need for further abatement.

There do not appear to be radical changes in the abatement technologies for the chlorine and titanium dioxide industries. For titanium dioxide production, the extent of abatement is largely dependent on the quality of the ore used.

This report also includes a review of the industry sector markets and economic performance, including process economics. In the late 1980s and early 1990s "globalization" of the chemical industry lead to intense price competition and to many companies reducing the number of chemicals they manufactured with the aim of concentrating on "core" products where they could become industry leaders.

Typically, the chemical industry is subject to economic cycles and the globalization tended to coincide with a down turn in the cycle so that profitability in the chemical sector as a whole, including the industry sectors dealt with by this report, was very low. Since 1994, however, profit margins have improved generally in line with an upturn in the industry. In the chlorine production sector recent higher prices have considerably improved margins although chlorine consumers have felt the effects of these higher prices.

Margins on medium concentration nitric acid production have also improved in line with a cessation in the long decline in fertilizer production. Returns on concentrated nitric acid have also continued to rise in line with improved UK economic activity in the industrial and metals sectors.

Margins relating to titanium dioxide have also recently improved following very poor results in the early 1990s. Sulphuric acid continues to provide modest returns.

On the whole, the bulk inorganic acids are characterised by modest returns on capital, whereas specialities (e.g. phosgene) are able to provide better returns.

There have also been major changes recently in the structure of the industry, and its ownership.

Key Words

Sulphuric, nitric, halogens, titanium dioxide, chlor-alkali, mercury, asbestos, SO_2, NOx , particulates.

1. INTRODUCTION

1.1 Background

This report provides information on pollution abatement and control techniques that apply to inorganic acid and halogen production processes. The information will be used in the revision of the Chief Inspector's Guidance Notes on inorganic acid and halogen processes.

Guidance Notes were produced by Her Majesty's Inspectorate of Pollution in order to assist its Inspectors in the authorisation and regulation of processes prescribed for Integrated Pollution Control.

There are currently four guidance notes covering inorganic acid and halogen processes:

IPR 4/10	Processes for the Manufacture, Use or Release of Oxides of Sulphur and the Manufacture, Recovery, Condensation, or Distillation of Sulphuric Acid or Oleum
IPR 4/11	Processes for the Manufacture or Recovery of Nitric Acid and Processes involving the Manufacture or Release of Acid-forming Oxides of Nitrogen
IPR 4/13	Processes for the Manufacture, or which Use or Release Halogens, Mixed Halogen Compounds or Oxyhalocompounds
IPR 4/14	Processes for the Manufacture, or which Use or Release Hydrogen Halides or any of their Acids.

These guidance notes are scheduled for revision and publication in 1997/ 1998. The Environment Agency intends to consolidate these Guidance Notes into one, with the aim of minimising repetition. This report provides technical and economic information to support updating.

Titanium dioxide manufacture is covered in separate Guidance Notes (4/10 and 4/13) as the primary methods of production involve either recovery of titanium dioxide from its ore using sulphuric acid to digest the titanium bearing ore or using chlorine to attack the raw material feedstock. In this report titanium dioxide production is reviewed separately (see Section 5).

1.2 Objectives of the Report

The primary objectives of the report are:

1. To provide updating information on the best available techniques for abatement and releases achievable worldwide for the selected processes.
2. To provide economic information for the appropriate UK Industry sectors.

1.3 Report Structure

The results of the desk study are contained in Sections 2 to 9. Section 2 contains reviews of different methods of sulphuric acid manufacture and abatement methods for sulphur dioxide.

Section 3 provides a review of the processes for manufacturing medium and concentrated nitric acids and the primary abatement techniques.

Chlorine, halogen and halide compounds are reviewed in Section 4.

Both processes for the production of titanium dioxide are reviewed in Section 5.

Section 6 provides a review of general pollution techniques, common to most production processes e.g. process control, instrumentation control, housekeeping to establish recent changes.

Section 7 covers monitoring, whilst section 8 focuses on the market situation/process economics associated with the various industries and the impact of abatement costs.

Section 9 provides an overview of sustainable development.

1.4 Brief Description of the Industry Sectors

1.4.1 Overview

In general, all the industry sectors covered by this study are mature, with well developed processes, in which older processes operate side-by-side with newer processes. Plants are often provided as part of an integrated production facility in which the inorganic acid or halogen process is either a raw-material for or a by-product of the process. Examples of these are:

- Generation of chlorine for direct use in PVC manufacture via vinyl chloride monomer
- Production of fluorine for use in making uranium hexafluoride for the nuclear industry
- Production of sulphuric acid as a by-product of metallurgical smelting.

Observed industry/country trends have also been reported. Examples are:

- Use of only the membrane process for chlorine production in Japan.
- Use of only the chlorine process for titanium dioxide production in the USA.

Assessment of the economics of these processes has, of necessity, to take into account the extent of integration with other production processes.

1.4.2 Sulphuric Acid

'Sulphuric acid is a very reactive chemical, capable of dissolving most metals and, in concentrated form, it is a powerful oxidising and sulphonating agent. It has a strong affinity for water and is used as a dehydrating agent. Sulphuric acid is widely used in the production of fertilizers and inorganic chemicals such as phosphoric acid, ammonium sulphate and titanium dioxide. Other uses include textile fibres, explosives, dyes, metals recovery and metals processing (pickling, etching and electroplating) and as a component of lead acid batteries.

Sulphur trioxide as a liquid or as oleum (a solution of sulphur trioxide in concentrated sulphuric acid) is used primarily as a sulphonating agent in making detergents.

The four principal routes to the manufacture of sulphuric acid, reviewed in this report, are:

1. Direct combustion of sulphur to sulphur dioxide, followed by the catalytic conversion of SO_2 to SO_3 and then absorption in 98-98.5% sulphuric acid
2. Recovery of SO_2 from metallic ore smelting by conversion to $_3SO$ and thence sulphuric acid, after cleaning and removal of impurities arising from the Smelter process.
3. Concentration of spent sulphuric acid, which is generated in a number of processes, e.g. the organic chemicals and petroleum refining industries.
4. Decomposition of dilute spent sulphuric acid, arising from chemicals processing and subsequent recovery and conversion of SO_2.

1.4.3 Nitric Acid

Commercial manufacture of nitric acid is achieved by the oxidation of ammonia. Two grades are generally produced

- medium concentration nitric acid (57-67% by weight).
- concentrated acid (up to 100% by weight).

Nitric acid is a product of considerable industrial importance and it is manufactured in large tonnages. The greater part of the production is used in the manufacture of fertilizers. Other significant uses are in the manufacture of polyurethanes, fibres, explosives and the treatment of metals.

As a consequence of the large tonnages used in downstream applications, and of the complexities of transportation, nitric acid plants are usually located close to user plants and may also be close to the ammonia feedstock source. Integrated complexes may influence nitric acid plant design in terms of heat integration between units and energy recovery.

1.4.4 Halogens/Halides

The dominant halogen produced and used in industry is chlorine. It is inextricably linked to caustic soda production through the chlor-alkali industry. Supply and demand between chlorine and caustic is often a balancing act and is the primary influence on the economics of chlorine production.

The major chlorine markets are:

- Vinyl chloride monomer (VCM)
- Pulp and paper industry, as a bleaching agent
- Propylene oxide
- Chlorinated hydrocarbons
- Phosgene
- Water treatment
- Titanium dioxide

There are three major production routes for chlorine. They are all variants of the electrolysis of brine to produce chlorine, hydrogen and caustic soda. The processes are the mercury cell process, the diaphragm process and the membrane process. The first two processes produce particular abatement problems; e.g. mercury and asbestos (the diaphragm). These problems are reviewed in the relevant Sections of this report.

In respect of the other halogens, the manufacture of bromine in the UK is by extraction from seawater, by acidification with sulphuric acid. Primary uses are:

- In ethyldibromide, used as a lead scavenger additive in gasoline. With the phasing out of lead in gasoline this is likely to be a declining usage.

- Inorganic metal bromides are used as hydraulic fluids in the oil drilling industry.

- Bromine based fire retardants (currently a growing market).

Iodine is not manufactured in the UK but has significant use as a dietary supplement, in catalysts, inks, pharmaceuticals, photographic equipment and sanitary and industrial disinfectants.

The only commercial route to fluorine manufacture is by the electrolysis of an anhydrous potassium bifluoride and hydrogen fluoride mixture. Fluorine is the most reactive element combining readily with most organic materials at, or below, room temperature. It is difficult to transport and is used largely in situ, in integrated facilities e.g. for uranium hexafluoride manufacture.

Primary uses include:

- Production of uranium hexafluoride, used in the nuclear industry to separate out the uranium isotopes by gas centrifuging.

- Sulphur hexafluoride for high voltage electrical insulation.

- Production of hydrogen fluoride for subsequent use in the production of "alkylate" for gasoline blending.

- Fluorocarbon polymers such as polytetrafluoroethylene.

1.4.5 Titanium Dioxide

Titanium dioxide is a highly stable compound and is classified as being a nuisance particulate, of low toxicity. The low toxicity has resulted in titanium dioxide becoming the primary white pigment world-wide, for paints, plastics and paper. These account for about 85-90% of usage. It should be noted however that titanium dioxide as used in the pigment industry is coated with various compounds to aid dispersion and durability. These may have an impact on toxicity.

Other uses include inks, vitreous enamels, in electrical circuit elements such as varistors, as a catalyst and as a ceramic sensor for oxygen in automotive exhausts.

The two production routes (chloride process and sulphate process) are described in this report.

1.5 Sources of Information

1.5.1 Environment Agency

The Environment Agency's National Library of Authorisations has been reviewed to provide information on the type of operations and the producers governed by Guidance Notes; IPR 4/10,11, 13 and 14. The process descriptions for each authorisation have provided a useful initial overview in most cases of operators' production processes.

The main sections investigated in the NLA were Sections 4.3a-f (acid processes) and 4.4a-e (processes involving halogens). These correspond to the descriptions given in the Environmental Protection (Prescribed Processes and Substances) Regulations 1991 (Statutory Instrument 1991/472). Section 4.6, which covers chemical fertilizer producers, was reviewed in order to track all nitric acid manufacturers. Additionally, smelting processes were viewed to ensure any operators producing sulphuric acid from smelter offgases were included.

An appreciation of total annual emission releases by operator was obtained by reviewing the Chemical Release Inventory generated by the Environment Agency.

1.5.2 Public Domain

Literature searches for sulphuric acid, nitric acid, halogens and titanium dioxide and related processes were carried out to explore the information relating to abatement technologies reducing their pollutant emissions. These searches used The Royal Society of Chemistry's Chemical Engineering and Biotechnology and the US Department of Environment's Energy Science and Technology databases.

The Internet was accessed and various web site addresses visited including the US EPA site. The Lycos and Yahoo search engines using appropriate keywords were searched. The following Japanese research establishment was accessed to investigate approaches to abatement techniques; National Institute for Resources and Environment http://www.nire.go.jp.

1.5.3 Europe

Euro Chlor Federation were contacted and a number of their publications reviewed in order to gain an insight into their perspective. Euro Chlor Federation represents all 38 western European chlorine manufacturers.

Discussions were held with Bayer AG (Uerchingen site) concerning their titanium dioxide plant, which is governed by extremely stringent waste discharge limits.

1.5.4 USA

Foster Wheeler used the resources of Foster Wheeler Environmental Corporation (USA) to obtain information on US emissions practice in sulphuric and nitric acids production, titanium dioxide manufacture and halogens manufacture. This information has been incorporated into the report in the appropriate sections.

1.5.5 Japan

Asahi Glass a leading membrane manufacturer provided information on membrane technology development and latest products.

1.5.6 Licensors

A questionnaire was sent to licensors covering nitric acid technology and abatement methods. Licensors contacted were BASF, Engelhard UK Limited, Weatherly Inc., Johnson Matthey, Espindesa, Uhde and Grande Paroisse. Chemetics (Canada) were contacted in order to ascertain their views on attainable emission levels and abatement possibilities. Responses were provided by BASF and Espindesa. A discussion took place with Simon Carves, UK licensee of the Monsanto sulphuric acid technology. Information was obtained on the Boliden process for treatment of liquid effluents from metallurgical acid plants.

ICI Katalco provided technical and a supporting proposed technical publication on HYDECAT™; a process for treating sodium hypochlorite.

1.5.7 Visits to UK Producers

Visits to UK producers were made following the issue of the first draft report (see Table 1.1). Without exception, the producer's representatives were very helpful and extensive background knowledge was obtained. Foster Wheeler wishes to express its appreciation of the hospitality and co-operation received.

The views contained in this report, however, are those of Foster Wheeler and should not be regarded, necessarily, as being supported by an individual company, or representing an individual facility.

Table 1.1: Visits to UK Producers

Company	Type of Plant	Date of Visit	Contact
Brittania Zinc	Metallurgical sulphuric acid	13/03/98	A. Nash
Lambson	Sulphuric acid	11/03/98	Dr. D. Anderson
Kemira Agro UK Ltd	Nitric acid	17/03/98	M. Burgess
Terra, Billingham	Nitric acid	19/03/98	D. C. Thompson D. Forrest S. Farnworth
Terra, Sevenside	Nitric acid	16/03/98	I . Craig
ICI Runcorn	Chlorine/sulphuric acid	31/03/98	I. Taylor
Rhodia Ltd	Chlorine/sulphuric acid	06/03/98	R. Malia (Section Manager Environment)
Associated Octel	Chlorine	18/03/98	P. Shields
Laporte Fluorides	Fluorides, hydrofluoric acid	12/03/98	P. Brockerton
William Blythe	Sulphites/iodates	08/04/98	C. Milner
Hays	Iron III chloride / polyaluminium chloride / hydrochloric acid	23/04/98	T. Wellington (Production Manager)
Millenium	Titanium dioxide via the chloride route	10/03/98	B.J. Crocker (Environmental Manager)
Tioxide, Greatham	Titanium dioxide via the chloride route	05/03/98	D. Aberdeen (Safety, Health & Environment Manager)
Tioxide, Grimsby	Titanium dioxide via the sulphate process	22/04/98	J. McClean

2. MANUFACTURE OF SULPHURIC ACID

2.1 Introduction

Commercial processes for virgin 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 multistage reactor.

The contact process can either be carried out with 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 re-generation or by concentration in multi-effect evaporators.

Oleum and purified sulphur trioxide are manufactured from the sulphur trioxide produced in the contact process. These processes are outlined in section 2.4.

2.2 Manufacture of Sulphuric Acid from Sulphur

2.2.1 Overview

The production process comprises three principal steps:

i) the combustion of molten sulphur to sulphur dioxide, with an excess of dried air:

$$S + O_2 \rightarrow SO_2$$

ii) conversion of SO_2 to sulphur trioxide by reaction over a vanadium catalyst with oxygen remaining after the combustion stage:

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$$

iii) absorption of SO_3 into the water contained in concentrated sulphuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

All of the stages are carried out at slightly above atmospheric pressure. The combustion and absorption stages are essentially irreversible. The conversion of SO_2 to SO_3, however, is a reversible reaction with the degree of conversion of SO_2 being limited by equilibrium. Emphasis is given in the design of plants to maximising SO_2 conversion, as unconverted SO_2 is discharged to the atmosphere as a pollutant and represents an economic loss. A particularly effective way of increasing SO_2 conversion is to carry out part of the absorption of SO_3 within the conversion stage. This is known as the 'double absorption' process.

Considerable amounts of heat are given out at each of the three stages; for example, a 1000 te/day plant liberates over 60 MW of heat. A significant proportion of total investment is associated with rejecting this heat efficiently, whilst keeping operating temperatures within required ranges. Part of the heat is recovered as steam.

Unconverted SO_2 emitted in the tail gas from the final absorption stage represents by far the largest emission to atmosphere. Smaller quantities of SO_3, sulphuric acid vapour and sulphuric mist are also emitted in the tail gas. Acid mist is formed by the reaction of SO_3 with water vapour and condensation of the sulphuric acid formed as very small particles; the mist is not removed by conventional scrubbing operations. There are no continuous liquid effluents.

2.2.2 Process Description

A simplified flowscheme of a single absorption plant is present in figure 2.1.

Air Drying

Admission of water (particularly water vapour) into the process could lead to the condensation of acid on cold metal surfaces (and hence corrosion) and to the formation of sulphuric acid mist. Once formed, sulphuric acid mist is difficult to remove and passes through the equipment as very fine droplets (<10 µm); emerging in the tail gas. Air used in the combustion of sulphur is therefore dried by contact with concentrated sulphuric acid in the packed drying tower. 98.5% acid is fed to the tower from the final and intermediate absorbers and this is diluted to typically 93% by absorbed moisture. The diluted acid can be returned to the absorbers, where it provides water for absorption of SO_3, or it can be exported as a product. Considerable heat is evolved in the drying process and this is rejected in an external cooler. To achieve low moisture contents in the dried air, the acid is cooled to 60-70°C. This should provide a residual moisture content of around 50 mg/m^3 in the dried air.

Dry air is then compressed to around 1.4 bar and is fed to the sulphur burner.

Sulphur Combustion

Molten sulphur is burned in excess air in the sulphur burner, a brick-lined furnace. The flow of air, which is controlled in proportion to the sulphur feed rate, must be sufficient to:

- provide oxygen for the oxidation of sulphur to SO_2;
- provide oxygen for the conversion of SO_2 to SO_3; and
- provide excess oxygen to drive the reversible conversion reaction towards SO_3.

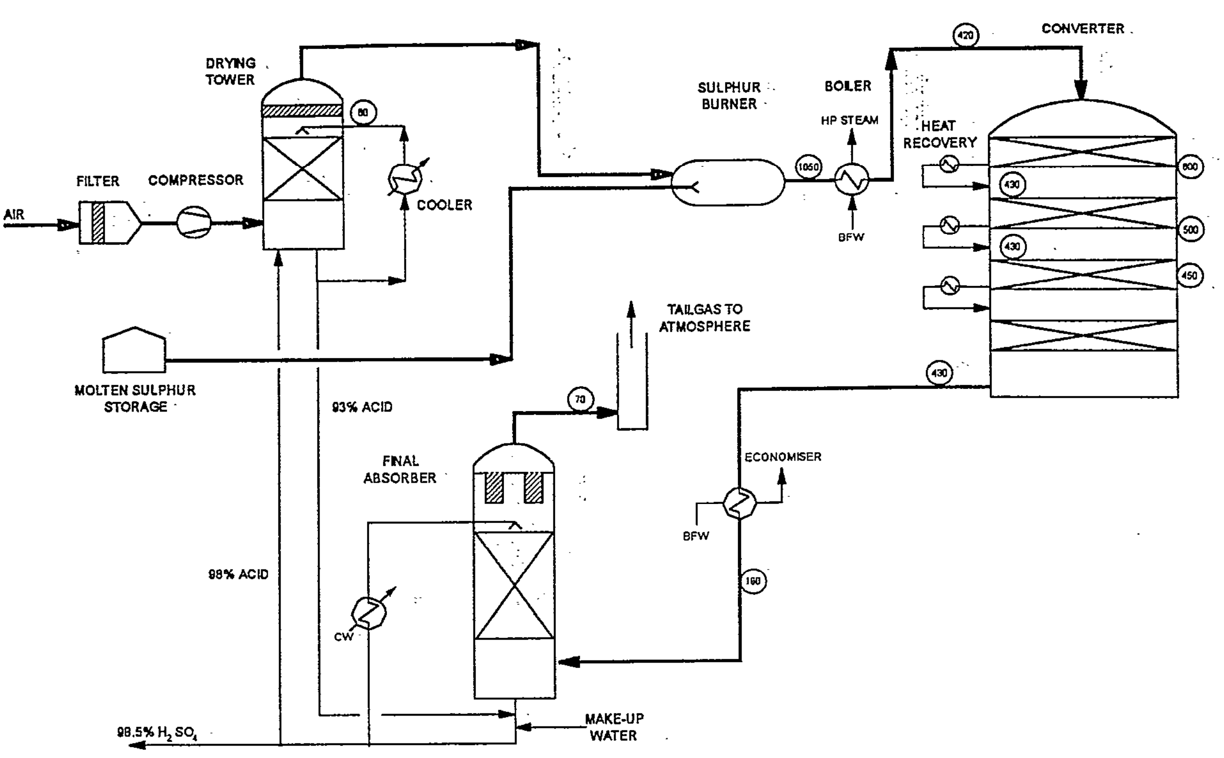

Figure 2.1: Single absorption process for sulphuric acid

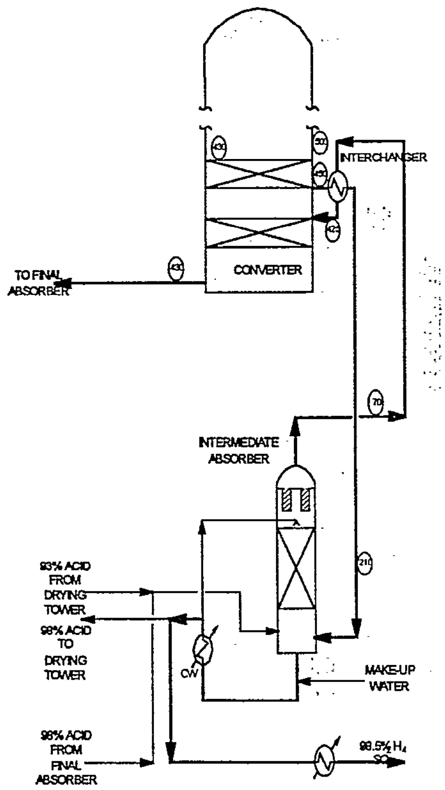

Figure 2.2: Intermediate Absorber

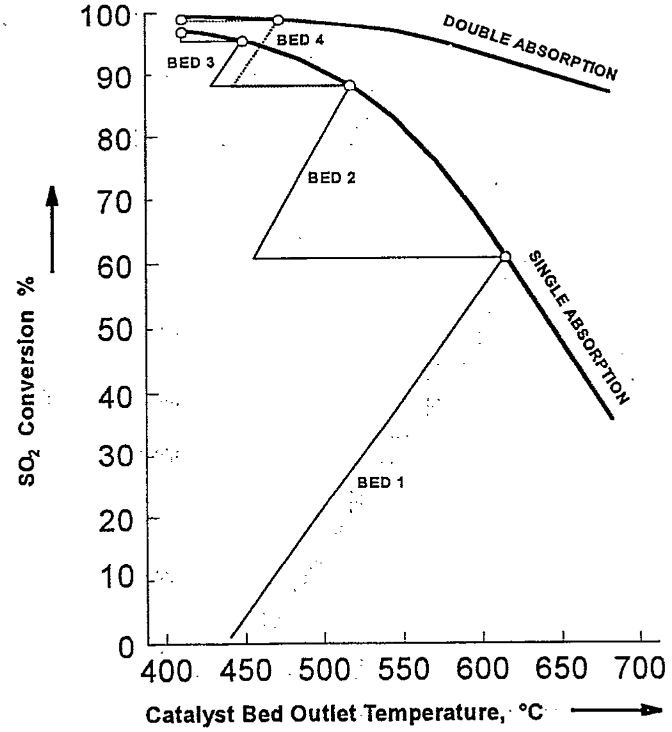

Figure 2.3. Comparison of single absorption and double absorption processes

Although the conversion reaction requires an O_2/SO_2 ratio of 0.5 molar, industrial practice is to use a ratio of 1/1 or slightly above. Typical conditions at the outlet of the sulphur burner are:

- SO_2: 9.5 vol%.
- O_2: 10.5 vol% (to give a ratio of 10:11)
- Temperature: 1000-1100°C.

Traces of SO_3 and nitrogen oxide are also present.

The SO_2 rich gas is immediately cooled to around 420°C in a waste heat boiler; raising steam at 50 bar or above. The cooled gas then passes directly to the converter.

Conversion

The oxidation of SO_2 to SO_3 takes place in the converter over a number of beds of a vanadium catalyst. The reaction is reversible and highly exothermic and conversion to SO_3 is favoured by low temperatures. It is therefore necessary to remove the heat released by the reaction between the catalyst beds. This is done by cooling the gas leaving a catalyst bed to the lowest temperature that the catalyst will operate at, before returning the gas to the following bed. The heat extracted is used to raise and superheat steam. 4 beds of catalyst are usual although 5 beds may be used to achieve slightly higher SO_2 conversions.

In converting a single absorption process to double absorption, an intermediate absorber is placed between the third and fourth beds (see figure 2.2). This removes the SO_3 formed by that stage and so allows further conversion of SO_2 to SO_3 in the final bed. In the single absorption flowscheme there is no intermediate absorption and so SO_2 conversion is limited and all SO_3 absorption occurs in the final absorber. Single conversion processes tend to be favoured where SO_2 concentrations are lower and far more variable eg. metallurgical SO_2. They are also utilised in older existing plants.

Figure 2.3 illustrates how SO_2 conversion efficiency changes between the beds and between single and double absorption. The double absorption process is now regarded as the standard process for new plant. Also many existing single absorption plants have or are being converted to double absorption.

The catalyst used is vanadium pentoxide promoted with potassium sulphate, supported on an inert material such as silica gel or a zeolite. Although fresh catalyst is capable of striking at 385°C, temperatures of 400-410°C are necessary for sustained operation. The catalyst is resistant to poisoning although it is deactivated by liquids and by operation at much above 600°C.

Catalyst doped with caesium salts (sometimes referred to as 'low-bite' catalysts) are capable of sustained operation at 380°C. This is favourable to the conversion of SO_2 and the increase in overall efficiency results in lower SO_2 releases to air. The doped catalyst is, however, more expensive and somewhat less active. Low-bite catalysts are likely, therefore, to require replacement more frequently.

Examination of the catalyst bed/conversion profile in figure 2.3, however, indicates that it is not necessary to replace all beds with the low-bite catalyst. It appears feasible to restrict its use to the final bed; still achieving the improved conversion.

The catalyst is generally formed into rings, which operate with lower pressure drops than pellets and are less liable to dust blockages. The pressure drop of the first catalyst bed rises with time as dust in the incoming gases is intercepted. It is therefore necessary to remove and screen the first bed on a regular basis, typically every 12-18 months. Blockage of the catalyst bed can lead to lowered SO_2 conversion. The ultimate life of the catalyst is around 10 years.

In summary, high conversions to SO_3 are favoured by:

- operation with an excess of oxygen;
- operation at the lowest feasible temperature;
- use of an active (low temperature) catalyst;
- effective heat removal and temperature control;
- removal of SO_3 by the Intermediate Absorber; and
- good gas distribution to the catalyst.

SO_2 conversions for different configurations of beds and for single versus double absorption are illustrated in Table 2.1.

Table 2.1 - SO_2 Conversion efficiency

	Single Absorption	Double Absorption
4 Bed	98%	99.5% - 99.7%
5 Bed		>99.7%
4 Bed Caesium Doped	99%	>99.7%

Absorption

SO_3 is absorbed in 98-98.5 wt% sulphuric acid in packed towers where it reacts with added water to form more acid. The sulphuric acid is circulated through coolers to remove the heat liberated.

To achieve the highest possible absorption of SO_3, it is necessary to control the temperature of the absorption process and the concentration of the circulating acid. 98.5% H_2SO_4 represents a composition at which the partial pressures of H_2O, SO_3 and H_2SO_4 are all minimums, thus favouring optimum absorption. Operation at other acid concentrations can lead to higher losses of SO_3 and H_2SO_4 vapour and to increased formation of acid mist. The 93% acid from the drying circuit is also returned to the circulating acid. Acid concentration is controlled by adding water to the acid circuit under automatic control. The temperature at the top of the absorbers is controlled at 60-80°C. In double absorption, 80-90% of SO_3 is absorbed in the intermediate absorber, which is therefore used to produce the 98% grade of acid. The final absorber also produces 98% acid normally, which is recycled to the intermediate absorber. The final absorber may be used to produce lower grades of acid. For example, if a 93% acid product is required, this would be taken from the final absorber acid loop. In single absorption plants, all the SO_3 is absorbed in the final absorber.

Over 99.9% of SO_3 formed in the converter is removed in the absorber(s).

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.

Acid mist formed in the absorbers and elsewhere in the plant is not removed in the absorbers. fibre bed mist eliminators, consisting of beds packed with glass or teflon fibres held between metal screens, are used to remove mist with very high efficiencies. These designs are capable of removing all particles of 1 micron or larger and can remove particles down to 0.2 micron at efficiencies of well over 95%.

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 intention is to have as many of the catalyst beds as practicable brought up to the catalyst "strike" temperature before SO_2 is admitted.

Direct firing has a number of disadvantages. These include exposing the catalyst (and the associated SO_3) to combustion products (water and hydrocarbons/smoke), although water damage to the catalyst can be avoided by operational means. 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.

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 4th catalyst bed and before the final absorber. This is satisfactory until the temperature of the 4th 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 should be considered as 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.

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 3rd and 4th beds if start-up emissions of SO_2 are to be minimised.

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 to 3 days, then enough heat should be retained within the plant and converter beds to permit the re-introduction of sulphur burning without prior pre-heating of the beds. For pre-planned short shut-downs, one means to maintain the bed temperatures is to allow them to rise prior to coming offline. 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.

2.2.3 Attainable Releases

UK and US limits are both based on the loss of sulphur in the stack. UK limits for existing and new plants are expressed in table 2.2 as a percentage loss of sulphur feedstock (as SO_2).

Table 2.2 - UK limits

	% Sulphur loss	Requirement to achieve
New plant	0.3	Double absorption, 99.7% conversion
Existing Double absorption	0.5	99.5% conversion
Existing single absorption	2.0	98% conversion

Improvements in releases from existing plant would therefore require either process improvements (as in 2.2.3 above) or use of abatement technology (see Section 2.6.3).

US emissions limits are:

2 kg SO_2/te 100% acid (ie the emission from a double absorption plant)

0.075 kg acid mist (as H_2SO_4)/te 100% acid (i.e. emission from very high efficiency absorption/mist elimination)

2.3 Sulphuric Acid From Metallurgical Processing

2.3.1 Overview

Commercially important non ferrous metals, including copper, lead, nickel and zinc frequently exist in the form of sulphide ores. The metal values are extracted by roasting the ore in air, to burn off the sulphur as sulphur dioxide, followed by a variety of metallurgical processes to recover the metal. Considerable quantities of SO_2 are released by roasting and the most economical disposal is by way of conversion to sulphuric acid.

After preliminary cleaning in the metallurgical plant, the off gases are subjected to a number of stages of further clean up at low temperature before being passed to the sulphuric acid converter. The converter and acid absorbers are similar to those used in the production of acid from sulphur but in this case the heat recovery around the converter is designed to accept a cold gas, rather than one at over 400°C as is the case with sulphur-based plants. The exothermic heat of reaction is therefore used to heat up the incoming gas. Generally there is little or no energy available for export. The whole of the acid plant must also be designed to accept a feed gas with a relatively low and variable concentration of SO_2.

A full description of the production of sulphuric acid and the variables affecting it is given for the sulphur-based process, to which reference should be made.

2.3.2 Source and Nature of the Off-Gases

A variety of processes (roasting, smelting, sintering) are used in the recovery of non ferrous metals from their sulphide ores. There is a variety of equipment used in such processes, including multiple hearth and fluidised bed roasters, reverberatory furnaces and flash smelters. In all of them, the objective is to recover the metal values by oxidising the contained sulphur to SO_2 at high temperature. Some of the heat required is provided by sulphur oxidation, but it is usually necessary to fire a supplementary fuel.

The amount of excess oxygen used in these operations varies between the process and equipment types and some of the processes are operated on a batchwise basis. The flow of off gases and their SO_2 content will therefore, vary with time.

Whereas in a sulphur-based plant, the concentrations of SO_2 and oxygen may be controlled accurately, their concentrations in metallurgical off gases are functions of the design and operation of the metallurgical processes involved. SO_2 concentrations from a multiple hearth roaster range from 1.5-3.0 vol%, from a fluidised bed roaster from 10-12 vol% and from a flash smelting furnace from 10-70 vol%. What is important from the viewpoint of acid production is that the SO_2 content is uncontrolled, is variable and tends to be lower than with sulphur burning plants.

Raw off-gases are generally subjected to pretreatment within the metallurgical plant so as to cool them (to about 200°C) and to remove the bulk of their entrained dust, either by a cyclone or an electrostatic precipitator.

Off-gases fed forward to the acid plant may contain the following types of impurities:

Dust	-	Solid entrained particulates which could clog the first catalyst bed in the acid converter.
Fumes	-	Aerosols of 0.01-2 micron diameter formed by the condensation of volatilised metal compounds (e.g. Zn, Pb, Sb, Bi, Cd and their chlorides, sulphates and oxides) as the gas is cooled to 300-400°C.
Volatile Metals	-	Similar to fumes, except that they have much lower condensation temperatures, often close to the gas saturation temperature. Includes As, Se, Hg and their chlorides, sulphates and oxides.

Note that arsenic and antimony deactivate the sulphuric acid catalyst.

Gaseous Impurities - Including SO_3, HCl, HF, CO, CO_2.

With the exception of CO and CO_2, these impurities must be removed before the off-gases are sent to the sulphuric acid plant.

2.3.3 Process Description

Gas Clean Up

The impurities contained in the off gases are removed by a combination of operations, usually based on cooling, scrubbing and physical separation. The design of the clean up system is adapted to the expected range of compositions of the off gases. A typical flowscheme is shown in figure 2.4.

Off gas from the metallurgical plant enters at 320-400°C and is quenched in a venturi scrubber to the adiabatic saturation temperature, 60-80°C. Large dust particles (over 10 micron), up to 50% of the SO_3 and less than 25% of the fume and volatile metals are absorbed. The circulating liquid becomes acidic through the absorption of SO_3.

Saturated gas is further cooled in the gas cooling tower, normally a packed column with external indirect cooling. Lowering of the gas temperature in this column permits the removal of water vapour from the gas (and hence allows a water balance to be maintained on the acid plant). Additionally, allowing volatile materials to condense helps the absorption of gaseous impurities such as HCl.

It may be necessary to purge the clean up system of impurities that have separated from the gas stream. The purge must be treated by neutralisation and sedimentation for removal of its acidic, suspended and dissolved components.

Cooled gas then passes to a wet electrostatic precipitator for removal of any solid and liquid contaminants still present in the gas.

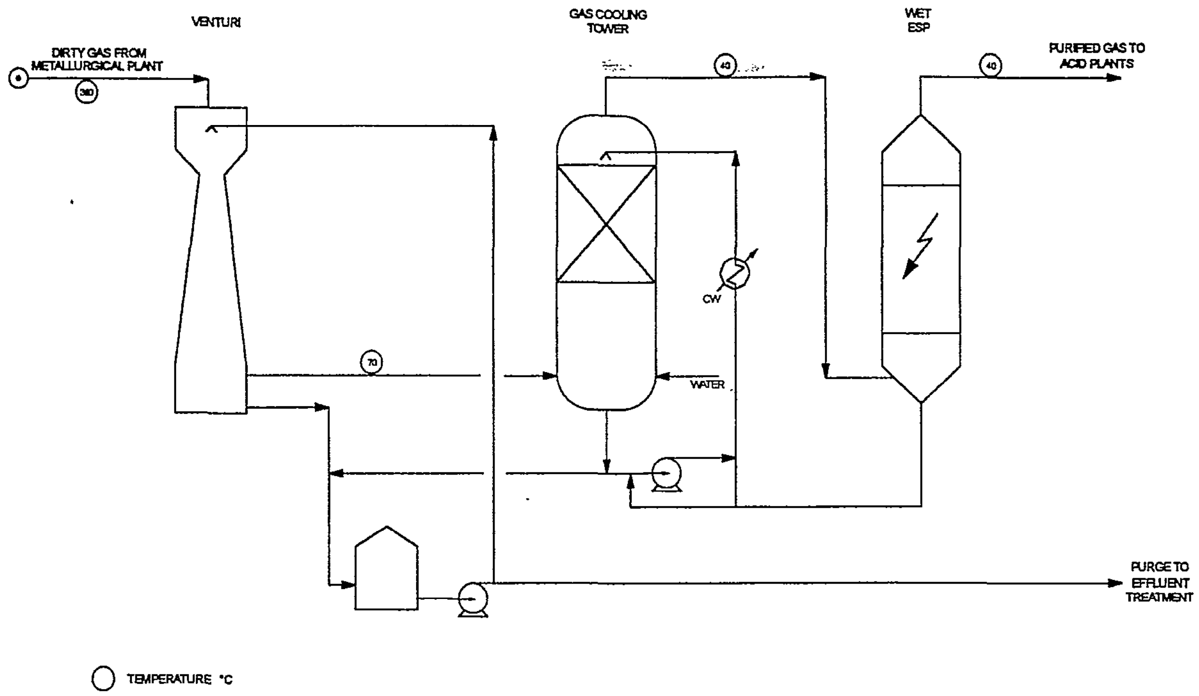

Figure 2.4 : Typical flowscheme for metallurgical gas clean-up

The removal of mercury and its compounds from the off gases presents a particular problem as, although metallic mercury may be removed by cooling and condensation, some will remain in the vapour phase. A number of techniques have been developed for mercury removal from the gas, including:

- Dry filtration with selenium impregnated filters.
- Filtration with activated carbon.
- Addition of selenium to the scrubbing liquid.
- Scrubbing with concentrated sulphuric acid (and reaction to mercuric sulphate).
- Scrubbing with mercuric chloride solution (and precipitation of mercurous chloride).

Alternatively, mercury may be removed from the product sulphuric acid.

Acid Production

Double Absorption Scheme

The flowscheme for sulphuric acid production from metallurgical processing is essentially the same as that for acid production from sulphur, except that:

- There is no sulphur burner and the O_2/SO_2 ratio in the off gases may need adjustment.

- The feed to the converter is cold and so heat rejected from the conversion step is all used to heat up the gas to 420°C.

Cleaned off gases free of dust and mist and containing 5-10% SO_2, but water saturated, enter the acid plant at ambient temperature. Air is added to bring the O_2/SO_2 ratio to 1.0 to 1.1 and the diluted gas passes to the drying tower, where it is dried by contact with 98% sulphuric acid. The gas clean up plant should be designed to remove sufficient water vapour to prevent the amount of water removed in the drying tower exceeding the stoichiometric requirement for acid production.

Dry gas at around 50°C is compressed to around 1.4 bara and then passes via a heat exchange network to the inlet of the converter at 420°C. All of the reaction heat given out in the converter is used to preheat the feed gas, therefore no surplus heat is available for the production of steam. A heat balance over the converter can only be maintained when the inlet SO_2 concentration remains above about 5%.

The intermediate absorber is normally placed between the second and third beds, unlike the sulphur-based flowscheme (between the third and fourth beds). As in the sulphur-based scheme, however converted gas will pass to a final absorber where sulphur trioxide is absorbed in concentrated acid. Unconverted SO_2 passes through to atmosphere.

Single Absorption Scheme

In the single absorption scheme, the heat balance over the converter becomes easier as heat is not rejected from the converter in the intermediate absorber. This allows a heat balance to be maintained at down to only 2 vol% SO_2, but with such dilute feed gases the amount of water introduced in the feed exceeds that needed for 98% acid production. Single absorption plants therefore tend to be used with dilute off gases. It still may be practicable to attain SO_2 recovery levels similar to those achieved with double absorption by using high O_2/SO_2 ratios (ca 1.7) and caesium-doped catalysts.

2.3.4 Releases

The releases to atmosphere from double absorption plants are similar to those from sulphur-based double absorption plants. As noted above, single absorption plants operating on dilute off gases should achieve similar SO_2 emission levels on a concentration basis.

In addition to gaseous emissions, metallurgical acid plants also generate solid and liquid wastes. The liquid purge from the gas clean up section is treated for the neutralisation of contained acid and the precipitation of dissolved and suspended materials. Limits are placed on the concentrations of ions in the treated purge liquid for discharge to surface waters. Some comparative limits are given in Table 2.3. Where practicable the first sludges separated are recycled to the metallurgical plant for recovery of the metals.

Table 2.3 Release limits for aqueous discharges

	mg/litre	
	Germany(1)	USA(2)
As	0.1	4.0
Cd	0.2	0.5
Hg	0.03	*
Cu	0.5	3.9
Pb	0.5	0.8
Zn	2.0	2.7
Fe	3.0	*
Se	1.0	*
Cl^-	*	*
F^-	50.0	127.0
SO_4^{2-}	400.0	*
Suspended solids	0.5	76.6
pH	6.4-8.5	7.5-10.0

(1) For copper smelters

(2) Regulations specify mg/kg 100% acid, above numbers calculated by assuming that discharged effluent is 0.4 m^3/ton acid

* Not specified

Precipitated solids, consisting of metals in non-leachable form, must be disposed of to special landfills.

2.4 Manufacture of Oleum and Sulphur Trioxide

2.4.1 Manufacture of Oleum

Oleum, or fuming sulphuric acid, is sulphuric acid containing sulphur trioxide in excess over the formula H_2SO_4, e.g. 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 may be made in a single packed tower while 40% oleum is normally generated in two series towers. In a double absorption plant the extra equipment would be located before the intermediate absorber. Oleum concentrations in excess of 40% oleum are usually obtained by mixing liquid SO_3 with a low concentration oleum.

Sulphur trioxide is absorbed in a circulating stream of oleum, in which the 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% SO_3 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 be released 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 will be required to prevent external spillage, fume emission and moisture ingress.

Special attention is required in the handling and storage of oleum, since exposure to air is likely to release large quantities of fine sulphuric acid mist. Quickly deployable measures to safeguard against such releases should be available. 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 high enough to prevent condensation and solidification of SO_3. In practice this requires steam-tracing or high integrity electric-tracing to be installed, coupled with lagging to a high standard, such that all piping and fittings are maintained at or above 80°C. Temperature, pressure and current (for electric tracing) monitoring or data logging may be required with a trace heating failure alarm.

2.4.2 Manufacture of Liquid Sulphur Trioxide

Liquid sulphur trioxide is normally 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 returned to the oleum absorber for further sulphur trioxide addition and re-use.

Potential release routes

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

Release into air

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

Release into water

- Effluent from absorption column mist collection equipment.

Release to land

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

2.5 Manufacture of Liquid Sulphur Dioxide

2.5.1 Introduction

Liquid sulphur dioxide is normally manufactured by one of two methods:

- Partial condensation.
- Reaction of sulphur trioxide with liquid sulphur.

2.5.2 Partial condensation

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

The plant inlet gas is provided by taking a side stream from the sulphur dioxide rich feed gas stream to the sulphuric acid plant. This is taken 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 most of the sulphur dioxide.

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

Potential release routes for condensation process

None.

2.5.3 Reaction of Sulphur Trioxide with Liquid Sulphur

This method is more complex than compression-liquefaction and has the advantage of producing a very pure material without the requirement for compression. The process would normally be integrated within an oleum producing plant.

Molten sulphur is fed continuously with the 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.

Bituminous impurities, which may enter the reactor with the sulphur, tend to foam upon sulphonation and should therefore be purged periodically from the system. One method of purging is to remove the entire reactor contents after about 2000 hours of liquid sulphur dioxide production. The purge will be the main effluent from this type of plant.

Sulphur trioxide vents should be returned to the absorption tower(s) on the sulphuric acid plant, and sulphur dioxide vents to the converter inlet.

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

Potential release routes for reaction process

Release into air

- Release of sulphur oxides upon draining reactor contents.

Release into water

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

Release to land

- Contaminated excess sulphur settled out from spent reactor contents/purge.

2.6 Spent Sulphuric Acid Concentration

2.6.1 Source of the Spent Acids

One method of regenerating spent sulphuric acid is by concentration of the spent acids. The method is primarily used for acids with low levels of organic contamination and low acid concentrations.

Spent acid often arises from the use of sulphuric acid as an acid catalyst or as a dehydrating agent. Examples of the sources of spent acid that are processed by concentration are:

- Gas drying and purification (e.g. methyl chloride, chlorine).
- Manufacture of explosives such as TNT.
- Nitro benzene manufacture.
- Nitric acid dehydration.
- Manufacture of pesticides, organic intermediates and dyestuffs.

The concentration of sulphuric acid in the spent acid can range from 10 to 70 wt%, and in the concentrated acid from 50 to 98 wt%.

2.6.2 Process Options for Concentration

To be suitable for concentration spent acids contain either:

- little or no inorganic contaminants (which would build up in the concentration cycle); or
- up to 10% organic contaminants which are either volatile or easily oxidisable.

Plants for acid concentration can be classified as:

i) Evaporation in single or multiple effect evaporators operating at atmospheric pressure or partly under vacuum;

ii) Evaporation by direct contact with combustion gases and;

iii) Evaporation by indirect contact with combustion gases.

The trend in new plant construction has favoured multiple effect evaporation under vacuum. Although this is high in capital cost, high acid concentration is achieved at low fuel consumption. The process also facilitates the recovery or destruction of organic contaminants.

Multiple Effect Evaporation

In multiple effect evaporation, heat efficiency is achieved by carrying out the evaporation of water in stages. The vapour generated in the higher temperature stage is condensed to provide the latent heat requirements in a subsequent lower temperature stage.

A generic flowscheme for a 3 stage system is shown in figure 2.5 in which vapour from the second effect is used to reboil the first effect. The exact nature of the scheme used for a given spent acid will depend on the concentration and contamination of the spent acid and the desired concentration of the concentrated acid.

Spent acid is firstly pretreated for removal of volatile organic contaminants in the Acid stripper and the stripped organics are condensed from the stripper overhead. Either indirect heat transfer (as shown) or live steam injection may be used to provide the stripping vapour.

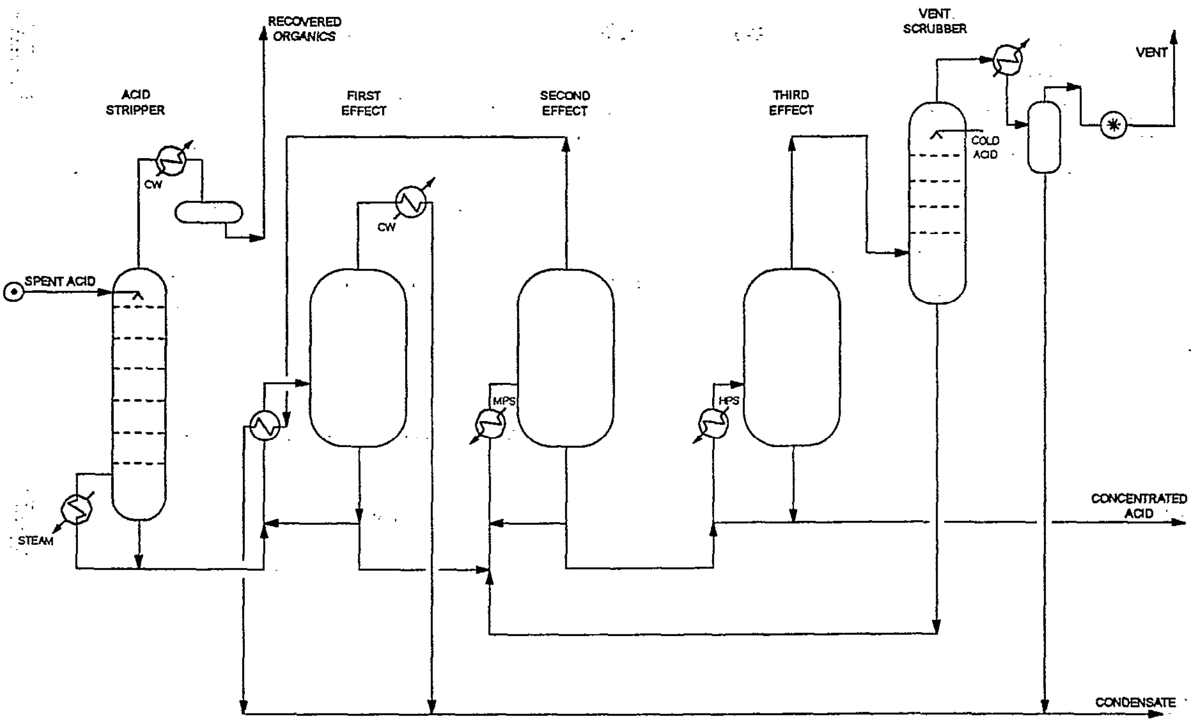

Figure 2.5 : Multi- effect evaporation

The stripped liquor then enters the first stage where partial evaporation occurs in a shell and tube vaporiser using condensing vapour from the second effect. The vaporiser may be natural circulation design (as shown) or forced circulation. Vapour generated in the first effect is condensed in an overhead condenser. The heat transfer surface in the vaporiser is generally fabricated in tantalium which is capable of withstanding the corrosive conditions at the temperatures involved.

Acid from the base of the first effect then flows to the second and then the third effects, which operate at successively higher temperatures, higher acid concentrations and lower pressures. The final effect might operate at over 200°C and at 90 mbar to allow 97% acid to be produced.

An oxidant, such as hydrogen peroxide may be injected into the system to oxidise non volatile organics to water vapour, CO and CO_2. Where nitric acid is used as the oxidant, 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. Vapours leaving the third effect are cooled and scrubbed against cold acid in the vent scrubber, for removal of sulphuric acid vapour and any inert gases are compressed in a vacuum pump, or steam ejector, before passing to atmosphere.

Metal contaminants will not generally be removed by the concentration process. Any ferrous ion, however will be oxidised to ferric form and will accumulate as a sludge. This will require subsequent removal, handling and treatment.

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

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

Direct and Indirect Contact Combustion Processes

In these processes heat for the evaporation of water is provided either by direct or indirect contact with combustion gases.

In the direct contact process, flue gases at around 600°C enter the first concentration chamber where they pass through acid at approximately 93% concentration. The cooled flue gases then pass in counter current flow to the acid through two more stages of concentration. The evaporators are constructed in brick-lined steel. A serious drawback to the process is the large amount of contaminated waste gas that is produced, which is difficult and expensive to clean up. Purification usually consists of scrubbing plus liquid droplet removal. The treated gases will still contain a significant concentration of sulphuric acid vapour (75-200 mg/m^3) and organic contaminants, originating in the spent acid.

In the indirect process, acid is boiled in a pot suspended in a furnace. The pot is surmounted by a scrubbing tower, which uses the spent acid to cool the hot vapours and condense out sulphuric acid present. Typically, for a spent acid concentration of 70%, the acid concentration will have increased to over 80% by the base of the tower. The final acid concentration achieved in the pot will be typically 95% or above, corresponding to a boiling temperature of at least 330°C at atmospheric pressure.

For older processes, the pot is likely to be fabricated of high silicon iron with a service life of 3-5 years. There is however a possibility of catastrophic failure with the material.

Organic impurities in the spent acid will be decomposed in the pot, either by the high temperature of operation or by the addition of an oxidising agent, such as nitric acid.

Vapour leaving the top of the scrubbing tower at around 130°C still contains as much as 1% sulphuric acid vapour together with nitric oxide, organic substances and the products of decomposition of organic contaminants. Waste material is condensed, but the residual non condensible components will require further cleaning. The quantity of gases requiring purification is much lower in this process, than with direct contact evaporation.

In view of the increasing stringency of environmental legislation, it becomes more and more difficult to justify the use of these outdated processes.

2.7 Sulphuric Acid by Decomposition of Spent Acid

2.7.1 Overview

Decomposition is generally applied to fairly concentrated acids (65-70% H_2S0_4 or higher), containing substantial amounts of organic impurities. Preconcentration of weak acid prior to decomposition may be used, although this would be a very costly operation.

Spent acid is decomposed at high temperatures to SO_2, water and oxygen. After cleaning, the decomposition off gases are used as the feedstock to a conventional sulphuric acid plant. The design and operation of such a plant and the factors influencing emissions are fully described for a sulphur-burning plant and so are not repeated here.

2.7.2 Source and Nature of the Spent Acid

The majority of spent acid arises from the operations of the organic chemical and petroleum refining industries. The composition of some important spent acids are tabulated below.

Table 2.4 - Spent acid compositions

Source	H_2SO_4 wt%	$(NH_4)_2SO_4$ wt%	H_2O wt%	Organics wt%
Alkylation	88-92		4-6	4-6
Nitration	65-70		20-35	1-5
Methyl Methacrylate	15	47	30	8

2.7.3 Process Description

Overall Scheme

The production of sulphuric acid from spent acid comprises the following main stages:

1. Decomposition of spent acid by spray burning in a direct-fired combustion chamber with supplementary firing to give controlled temperature and excess oxygen.
2. Heat recovery, including combustion air preheating.
3. Clean up of the SO_2 containing gases, principally to remove particulates and excess water.
4. Oxidation of SO_2 and absorption of SO_3 into concentrated acid in a conventional acid plant.

A simplified flowscheme for a spent acid decomposition plant is presented in figure 2.6.

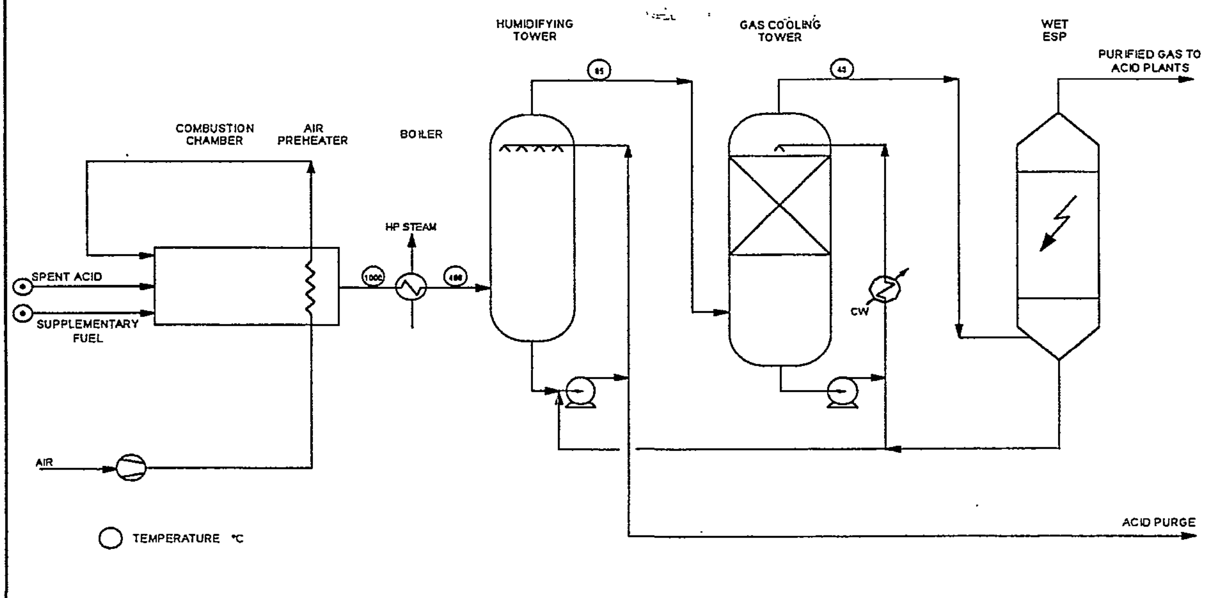

Figure 2.6 : Spent acid decompositon and clean-up

Combustion

Spent acid is sprayed into the combustion chamber with a controlled quantity of air. A temperature of around 1000°C is attained and a free oxygen concentration of 1.5 to 2.5 vol%. Under these conditions and with the residence time provided, virtually complete decomposition of sulphuric acid to SO_2, water and oxygen is achieved. The decomposition reaction is endothermic and heat must also be supplied to evaporate the water in the spent acid. Unless the spent acid contains sufficient combustible organic material, supplementary fuel must also be fired. This may be sulphur, H_2S or a high sulphur fuel oil (all of which tend to increase the SO_2 concentration) or some other convenient fuel, such as natural gas.

The water content of the spent acid has a critical effect on the design and operation of the plant. As the water content of the acid increases the amount of supplementary fuel fired must be increased so increasing the quantity of combustion chamber off-gases (and hence reducing their SO_2 content) and increasing the amount of water that must be removed in the gas clean up section. A point is reached (at 65-70 wt% H_2SO_4) beyond which the SO_2 content of the off-gases will no longer sustain autothermal operation of the converter in the acid plant. This corresponds to an SO_2 concentration of around 3 vol%. A number of strategies can be employed to deal with dilute acids:

- Preconcentration of the acid.
- The use of oxygen or oxygen enriched air.
- Burning sulphur or H_2S as supplementary fuel.
- Refrigeration of the off-gas in the clean-up section so as to condense out more water.
- Preheating of the air to 450-600°C (as shown in the flowscheme).

Off-gases are cooled to 350-450°C in a waste heat boiler which generates high pressure steam. The gases then pass to the clean-up section.

Clean-Up

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

After leaving the boiler, the gas enters a humidifying spray tower. Large particulates and up to half of the SO_3 are captured in the circulating weak acid solution. The remaining SO_3 is cooled to below its dewpoint and leaves the tower at around 65°C as an acid mist entrained in the gas stream.

The saturated gas is then cooled in a packed gas cooling tower to reduce the water content to about 1 mole per mole of SO_2. Alternatively, a graphite shell and tube exchanger may be used.

Final clean up is by an electrostatic precipitator, which removes the acid mist and remaining particulates.

Acid Production

The flowscheme for SO_2 oxidation and SO_3 absorption is very similar to that based on metallurgical off-gases.

Cleaned gas is mixed with additional air to adjust the O_2:SO_2 ratio and is then dried by contact with 98% sulphuric acid in the drying tower. Dried gas is compressed to 1.4 bara before being heated to 420°C by interchange with interbed flows and passing to the first catalyst bed in the converter. As in the scheme based on metallurgical off gases, all the reaction heat given out in the converter is needed to preheat the feed gas and so there is no possibility of raising steam. It is possible that the heat balance on the converter, especially with dilute feed gases, can be assisted by heat taken from the combustion system. As with the metallurgical-based process a heat balance can only be obtained over the converter with SO_2 concentrations of 3% or over.

The intermediate absorber is placed between the third and fourth catalyst beds; the arrangement of interchangers and feed preheaters around the converter is typical only and other arrangements can be used.

2.7.4 Releases

The Gaseous emissions from the acid plant are similar to those from the sulphur-based or metallurgical-based processes.

A liquid effluent is produced in the gas cleaning section which consists of a weak sulphuric acid containing small quantities of suspended solids. This stream may be treated by neutralisation and filtration before discharge, the filtered solids being disposed of to landfill. The nature of the solids depends on the contaminants contained in the spent acid.

2.8 Sulphur Dioxide Abatement Methods

2.8.1 Introduction

Modern designs of sulphuric acid production plants use the double absorption flowscheme and achieve SO_2 conversions of 99.7% or more, equivalent to an SO_2 emission of 350 ppmv (1000 mg/m^3) or less. There are a number of older plants operating in the UK which use the single absorption flowsheet which achieves an SO_2 emission of around 2500 ppmv (7140 mg/m^3).

There are basically two options for reducing the emissions from single absorption plants:

- Convert to double absorption
- Remove SO_2 from the tail gas from the single absorption flowscheme.

2.8.2 Conversion to Double Absorption

Conversion of single to double absorption has been carried out in the US and continental Europe. As a minimum, this involves:

- breaking into the converter shell to extract and reinject partly converted gas after SO_3 absorption.
- rearrangement of heat recovery on the converter to provide high grade heat for reheating of gas from the new scrubber.
- addition of a new absorber and associated cooling system.
- in many cases, modification of the air blower and its driver to provide additional head.
- modifying the acid circuit to optimise product acid/water balance.

Whether or not it is feasible to do this depends on whether there is spare land nearby and also on the state of the existing plant. With older plants it may be necessary to install an additional bed of catalyst (in a separate vessel) or even to replace the whole converter. Conversion to double absorption is therefore expensive, especially for life-expired plants, and may involve an extended shut down.

2.8.3 Options for SO_2 Removal

There are several viable methods for clean-up and reduction of SO_2 content in the tail gas from the absorber. Some have been developed specific to the sulphuric acid industry; others have been used in the desulphurisation of flue gas from power stations. Processes may 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 either as 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.
- desulphurisation processes.

Activated Carbon Processes

In recent years commercial processes have been developed that remove SO_2 from tail gas by a low temperature adsorption process using activated charcoal. Under suitable reaction conditions, and in the presence of moisture and oxygen, the SO_2 is converted via SO_3 to sulphuric acid. The sulphuric acid is retained within the activated carbon.

The activated carbon is regenerated on-line by a periodic water wash, which creates a dilute sulphuric acid. The process effectively creates zero effluent as the dilute acid is recycled to the sulphuric acid circulation loop. There may, however, be water balance problems if the product acid is too weak. Anticipated life of the activated carbon is typically five years. Typical recovery efficiencies from the tail gas are in excess of 90% SO_2.

The activated carbon process is considered to be competitive with conversion to double absorption processes in retrofit situations or in new plant.

Perceived advantages in comparison with the double absorption process are:-

- higher energy export.
- minimal waste.
- less equipment and hence lower capital cost
- the plant can be started up more quickly without exceeding emission limits

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 hydrogen sulphite - SO_2 is extracted and then released by steam heating. The absorbent is regenerated.

Other solvents in use include sodium carbonate, citric acid, regenerative amine absorbents and sodium citrate. Essentially all the processes function in a similar way and involve an absorption/scrubbing stage followed by a regeneration stage in which the SO_2 is recovered and, where practicable, the solvent is regenerated.

Efficiency of SO_2 removal for these processes may be 95%+.

These "add" on processes offer the prospect of being simpler and cheaper than conversion to double absorption, whilst producing 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

Flue gas desulphurisation is characterised by very large volumes of gas and the large quantities of SO_2 to be removed.

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%. 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 drier. 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 drier 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 occur 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. There is, however no vapour plume nor liquid effluent. There are some solids requiring disposal. to landfill.

If the sulphuric acid plant is adjacent to a compound fertiliser plant, then it is feasible that the ammonium sulphate effluent from an ammonia scrubbing unit could be fed to the granulator.

The tail gases from a conventional single or double absorption plant are dry as the last stage in the production process involves passing the gas through a circulating stream of concentrated sulphuric acid (a very effective drying agent). 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 the reduced temperature will also reduce the thermal buoyancy of the plume. 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.

BAT

BAT for new sulphuric acid plant should be seen as utilising successfully commercialised processes to minimise releases of SOx from the tail gas. It is therefore feasible to consider combinations of techniques that offer scope for extensive reductions in emissions to atmosphere, even though the combinations may not have been linked together, in commercial operation.. Based on the review of processes a suitable combination could include:-

- double absorption process.
- utilisation of a "low-bite" catalyst.
- inclusion of a tail gas abatement system (eg. activated carbon, peroxide).

For existing single absorption plant, where there may be constraints on space, BAT should be considered as:

- either conversion to double absorption or use of a regenerative tail gas abatement technique, and
- the use of low-bite catalysts.

Cost of Abatement

Costs of abatement of sulphuric acid plants are discussed in Section 8, Economic Considerations. Cost data have been expressed in terms of SOx recovery per tonne of daily installed capacity of sulphuric acid.

3. MANUFACTURE OF NITRIC ACID

3.1 Medium Concentration Nitric Acid

3.1.1 Process Features

Virtually all commercial manufacture of nitric acid is by means of the oxidation of ammonia. The majority of the plants are constructed for the production of medium concentration nitric acid (57-68% by weight). The methods used to manufacture concentrated nitric acid differ from those used for medium concentration acid, since nitric acid forms an azeotrope at 68% concentration.

In chemical terms, there are three essential steps to the process:

Catalytic Oxidation of Ammonia to Nitric Oxide (NO)

This is achieved by passing ammonia vapour, mixed with air, over a catalyst. The catalyst is usually platinum based in the form of a woven or knitted gauze. The typical life of a catalyst gauze used in dual pressure service is four to five months.

The overall reaction is represented by:

$$4NH_3 + 5O_2 \leftrightarrow 4NO + 6H_2O$$

Many other reactions also occur. Small amounts of nitrous oxide (N_2O) are formed in side reactions and there is some yield loss from the direct oxidation of ammonia to nitrogen. All these reactions are exothermic. The selectivity of the reaction to N_2O and to N_2 are favoured by low catalyst temperatures.

Oxidation of Nitric Oxide (NO) to Nitrogen Dioxide (NO_2)

This reaction occurs in the presence of excess air in the stream from the reactor by the route:

$$2NO + O_2 \leftrightarrow 2NO_2$$

The forward reaction is favoured by low temperature and high pressure.

Absorption of Nitrogen Dioxide into Water

This reaction is represented by:

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

The reaction is exothermic; heat must be removed lest the reverse reaction be promoted, and, in the vapour phase, the reverse of the oxidation reaction.

These chemical steps, and the conditions required to promote them, govern the form of all modern processes. An outline of the process is shown in figure 3.1.

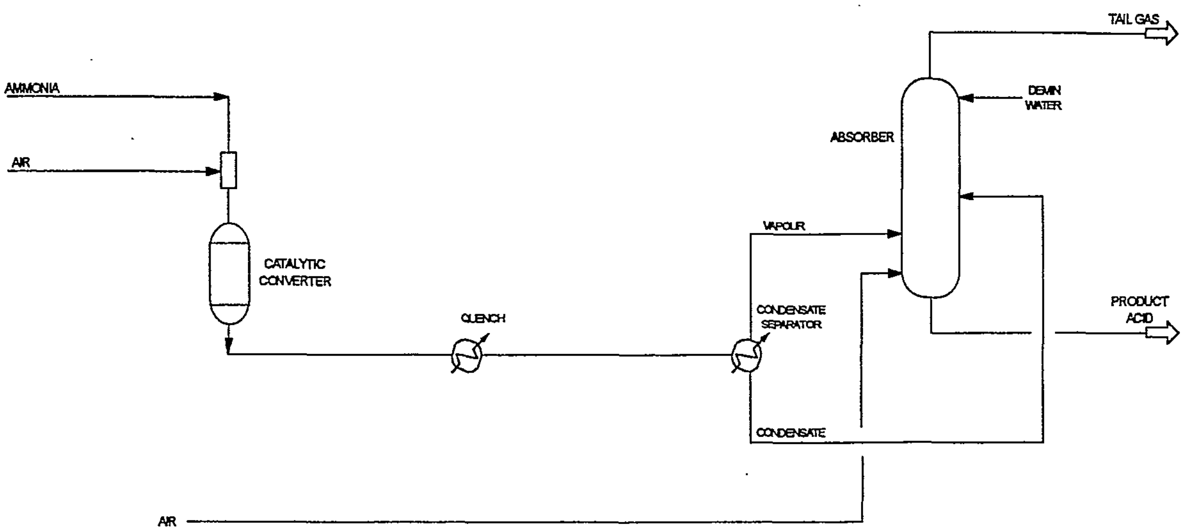

Figure 3.1 Basic process scheme for medium concentration nitric acid

3.1.2 Plant Design

The overall configuration of a plant to achieve these processes is generally the same. All processes have a catalytic converter unit in which the mixed air and ammonia stream is reacted. The gas flow passes to a cooling exchanger (sometimes referred to as the "quench") followed by a separator for the removal of condensate. The absorption of NO_2 to form nitric acid takes place in an absorption column where the gases are contacted counter-currently with water. Modern counter-flow absorption towers use high efficiency tray designs. 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.

The oxidation of NO to NO_2, is slow and because NO is practically insoluble in water the reaction occurs in the gas phase only. The reaction is also exothermic and the conversion of NO to NO_2 increases with falling temperature. Part of the oxidation therefore occurs in the system between the quench unit and the absorber, but the greater part of the reaction has to be achieved in the gas space of the absorber. To assist this process, supplementary air is fed to the base of the absorber.

The absorption reaction releases one mole of NO for every two mols of nitric acid produced. This has to be converted to NO_2 and then re-absorbed. Thus, increasing residence time is required in the absorber as the reaction progresses and accordingly the tray spacing increases towards the top of the column.

The acid flowing from the base of the absorber column is saturated with NO_2, which imparts a brown colour to the stream. The excess NO_2 is stripped from the acid in an extra column (bleach column) to decolorise the acid. This is achieved by contact with the supplementary air stream, which is then fed to the absorber column. The bleach column function is sometimes integrated as the bottom section of the absorber column.

During the reaction process small amounts of the catalyst vaporise. For this reason a collector is usually installed below the catalyst to capture this material. Gold or palladium may be used for this purpose as they form an alloy with the platinum and rhodium. The collector recovers 60-80% of the total catalyst losses. Sludge recovered from various items of equipment during shut downs may also have a significant metals content and is sent for metals recovery. Overall, therefore, only a small fraction of precious metal is lost.

Nitric acid plant design is a compromise of many factors. The key factors, governing design, are:

1. Choice of pressure and temperature for ammonia oxidation low enough to ensure good conversion and selectivity.

2. Choice of high enough pressure and low enough temperature in the absorption system to promote the oxidation of NO to NO_2, and the subsequent absorption and reaction of NO_2.

3. Arrangement of the various stages of compression, let-down and heat interchange to optimize heat and energy use and recovery.

4. Selection of materials of construction to suit the various conditions.

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

3.1.3 Principal Features of Licensed Processes

The development of the processes by different licensors and operators resulted in distinct variants on the central theme. The broad categories of process currently operating, worldwide, are:

1. Medium pressure processes operating at 3-6.5 barg.

2. High pressure processes operating at above 7.5 barg.

3. Dual pressure processes in which conversion is operated at 3-5 barg and absorption at above 7.5 barg.

The process engineering strategies were influenced by raw material costs, energy costs, capital costs and the associated costs of finance and by catalyst costs. The geographically influenced variations among these factors led initially to dual pressure processes being favoured in Europe and single pressure processes being the normal choice in the USA.

30-40% of the capital cost of a nitric acid plant is attributable to compressors, expanders, steam raising and heat interchange. The greater part of the energy used in compression is recovered within the process and the plants are usually net exporters of steam and/or energy.

Improvements in metallurgy, refinements of the design of heat exchanger networks, advances in compressor and expander design and in catalyst performance have led to a convergence of the economic parameters of high pressure and dual pressure processes so that the selection of process is often influenced by site specific factors related to site energy integration.

3.1.4 Energy Considerations

The heat and energy networks of nitric acid plants have been studied intensively and modern plants have highly integrated systems. Optimised conventional processes achieve a net power production of typically 175 kWh/te. One development has involved saturating the tail gas stream with water in order to optimise the power recovery and net power production of 230 kWh/te is claimed. The actual use that can be made of the power surplus depends on the local site conditions and explains why there are many variations in the type of drivers selected and choices between steam raising and power generation.

The performance of the turbines and expanders tends to be optimal only under the specified design flowsheet conditions. At relatively modest turn down conditions instabilities may develop in the turbine and expander operation. Sub optimal design may be required if variable outputs are expected.

A typical outline flowsheet for the now more usual dual pressure process is shown in figure 3.2.

The high integration of the energy recovery systems into the overall plant design has implications in retrofitting selective catalytic reduction (SCR) abatement systems. This will be covered later in section 3.1.7. Figure 3.3 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:

a) compress the process air, and
b) generate surplus electricity where practicable.

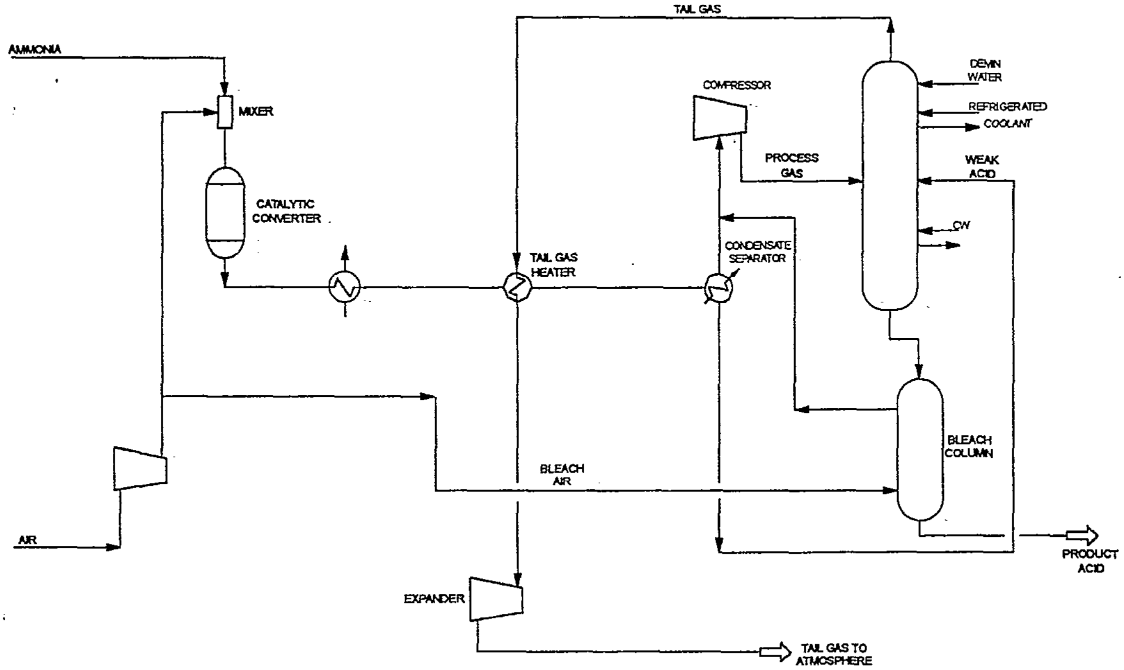

Figure 3.2 Simplified dual pressure flow diagram : medium concentration nitric acid

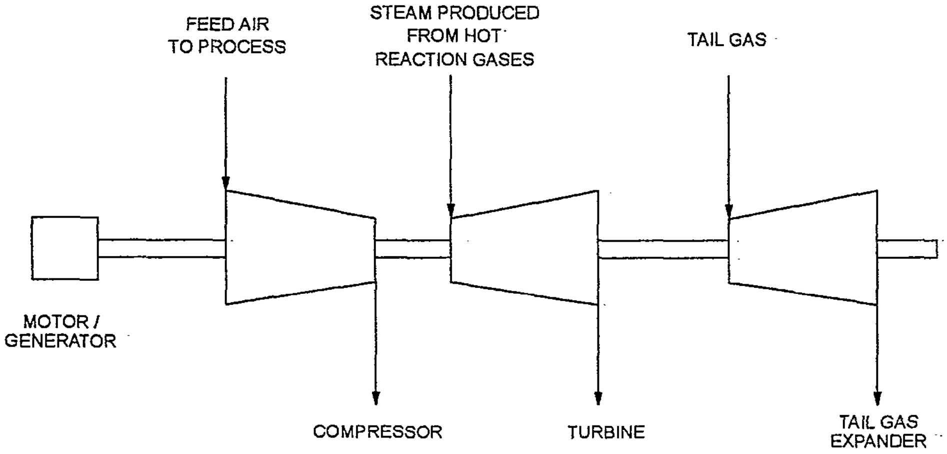

Figure 3.3 Simplified diagram of medium concentration nitric acid integrated drive train

3.2 Releases From the Process

3.2.1 Gaseous Emissions

The exhaust gases from the process are emitted in one stream which originates as the tail gas from the absorption column. The components of the stream are nitrogen, residual oxygen, nitrous oxide and acid forming oxides of nitrogen. The contributory feeds to the stream are the inlet air to the ammonia convertor and the stripping air injected into the bleach column.

The older plants were designed to optimise economic returns rather than to consider environmental performance.

Typically, the uncontrolled emissions from medium and high pressure plants contain 2000-4000 mg/m^3 of NOx (expressed as NO_2) which results in an emission factor for the product of 22 kg/tonne acid (expressed as 100% HNO_3) contained in a gas stream of around 3.9 tonnes/te 100% HNO_3. A small contribution to this total originates from the vent streams from compressor and expander rotary seal systems.

Nitric acid storage and loading activities make a small contribution to NOx emissions. Back venting from tanker to storage is normal good practice. The routing of vent lines back to the plant would normally incur heavy cost for little advantage.

Abatement techniques for minimizing NOx released are described in Section 3.6.

Fugitive emissions of ammonia also occur. These result from storage, handling and vaporising systems.

3.2.2 Liquid Effluents

There are no significant liquid releases directly associated with the process during normal production.

3.2.3 Solid Wastes

No solid wastes are released from the process during normal production.

3.2.4 Releases During Start Up, Shut Down and Other Transient Conditions

The highly integrated heat and energy network of the plant imposes a finite delay to the attainment of working temperatures and pressures. During this time there is an increased slip of nitrogen oxides through to the tail gases. This will occur with or without the use of abatement equipment. Transient releases of up to 1000 mg/m^3 NOx (as NO_2) may be experienced during start-up. There is a similar loss in purges during shutdown.

Diluted acid produced during start up is recycled to the process. Acidic wastes produced during wash out at shut down are neutralised and put to sewer. Ammonia slip during start up will react to form ammonium nitrate and this is purged from the system to avoid potential explosion hazard.

Spent catalyst and catalyst débris recovered from the reactor filter are returned to the catalyst manufacturer for metal recovery. Used air filters are disposed of as ordinary waste.

3.3 Abatement Techniques for NOx Emissions from Nitric Acid Plants.

3.3.1 General

These techniques are described in the context of medium concentration nitric acid plants. It will be appreciated that many of the techniques and considerations discussed are also applicable to other processes emitting nitric oxides.

Control techniques used for controlling NOx emissions fall into four broad groups:

- Extended Absorption.
- Catalytic Reduction.
- Chemical Absorption (Scrubbing).
- Adsorption.

A summary of the techniques, their impacts and applicability can be found in Table 3.1.

Table 3.1 - Summary of abatement techniques for nitric acid plants

Abatement Technique	Environmental Impacts	Typical NOx (mg/m^3)	Salient Features	Applicability
Molecular Sieve Adsorption	Extra fuel for regeneration.	20	High capital. Cyclic operation. Good turndown.	No recent examples of use of process. Can be added easily to existing plant.
Extended Absorption	Pumps and refrigeration require additional energy.	205 - 410	High capital if retro fitted; 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. Catalyst disposal and increased fuel consumption. (Potential for energy recovery).	205	High capital multiple beds with intercooling for low emissions - removes N_2O[1].	Tending to be superseded by SCR.
SCR	Ammonia slip and catalyst disposal.	100	Does not remove N_2O(1).	Easily added to existing plants.

Notes: (1) The decision to select between NSCR and SCR techniques may depend on the environmental impact of N_2O

3.3.2 Extended Absorption

Extended absorption, as its name implies, is designed to reduce emissions by increasing the efficiency of absorption. This may be achieved by introducing extra absorption capacity by:

a) the substitution of a larger tower for the existing column,
b) extending the existing tower with more trays,
c) the installation of a second absorber tower.

Sufficient gas phase volume is required to allow the oxidation of NO to NO_2 even with the extra absorption trays. It should be recognised, from the equation for the absorption reaction that for every three molecules of nitrogen dioxide absorbed, a further molecule of nitric oxide is released. An extended reaction volume is therefore required throughout the column for the re-oxidation of nitric oxide to occur.

Some variations in the use of extended absorption are:

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

2. Refrigeration of the coolant streams in the upper part of the absorption column. Vaporisation of ammonia may be used for this.

3. 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, reducing the total emissions to atmosphere. Second, an increase in the partial pressure of oxygen in the system increases the concentration of oxygen in the liquid film.

   The absorption of NOx in water to give nitric acid is the sum of two reactions:

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

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

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

$$2HNO_2 + O_2 \rightarrow 2HNO_3$$

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

3.3.3 Catalytic Reduction

Non Selective Catalytic Reduction (NSCR)

The non selective catalytic reduction process is used to convert NOx in the tail gas to nitrogen by reacting a reducing agent with the gas stream in the presence of a catalyst. The term non selective catalytic reduction refers to the reaction of the reducing agent, in which both the oxygen bound to the nitrogen and free excess oxygen present in the waste gas are reduced.

The process involves mixing a reducing agent with the tail gas over a catalytic bed. Part of the reducing agent may be used as an intermediate quench.

Reducing agents may be hydrogen and/or hydrocarbons such as natural gas, propane, butane or naphtha. They should be free from sulphur to avoid early deactivation of the catalyst (normally, platinum, rhodium and palladium on a support material such as alumina (AlO_3)). These catalysts generally have a long life and replacement is infrequent. The tail gas entering the catalyst bed should be at a temperature of 200-480°C, depending upon the reducing agent used, in order to provide good conversion efficiency and catalyst life. Hydrogen has the dual advantages of operating at the lower end of the temperature scale and does not introduce carbon monoxide into the tail gas. When hydrogen is sourced from an ammonia plant, however, availability will be restricted to periods when the ammonia plant is running. Loss of hydrogen will result in immediate loss of abatement. Any methane present in the hydrogen stream will also pass straight through the catalyst bed and out with the tail gas without reaction as the bed temperature is too low for the methane/ NOx reaction.

Two different reactions may take place:

- The reduction of nitrogen dioxide in the waste gas to nitrogen monoxide. This occurs when the amount of the reducing agent added is less than the stoichiometric ratio. This reaction merely results in a decolourisation of the waste gases.
- The reduction of the nitrogen dioxides in the waste gas to nitrogen. This occurs when the amount of reducing agent is in excess of that required to react with both the NOx and the oxygen contained in the waste gas. The gases leaving the catalyst reactor will contain substantially reduced concentrations of nitrogen oxides and oxygen and consist predominantly of nitrogen gas and water vapour. This step is the "abatement reaction".

The decolourisation reactions usually take place first, followed by the abatement reaction. Conversion efficiencies are typically 90% for the NOx gases and in excess of 90% for nitrous oxide.

Since the reaction of the reducing agent with the oxygen in the tail gas is exothermic, the gas leaves the catalyst at an elevated temperature, and may be used to raise steam and/or power via a gas turbine. Temperature rises of 160°C for hydrogen and 130°C for methane, naphtha, butane and propane may be anticipated for each 1% of oxygen burnt with the respective fuel. Since the maximum permissible operating temperature is typically 750°C, the maximum oxygen reduction per pass can be calculated.

It is common practice to reduce the oxygen levels in the tail gas to a minimum by carefully controlling the air flow in the Bleaching Tower, such that only one pass is required over the catalyst. Two stages of catalytic treatment are generally required when using methane as reductant, as it requires the highest catalytic operating temperature.

Selective Catalytic Reduction (SCR)

The selective catalytic reduction process is designed to reduce only the bound oxygen in the tail gas, with free O_2 only being reduced to a slight extent.

Since free oxygen does not have to be consumed, fuel requirements are lower, exit temperatures are lower and simpler and cheaper equipment may be used. The only commercially significant reducing agent used for SCR is ammonia.

Ammonia is completely mixed with the tail gas before being passed over a titanium and vanadium catalyst bed at a temperature of 350-800°C with typically a 95% reduction of NOx.

The basic reactions occurring in the reduction are:

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

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

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

Small quantities of ammonium nitrate and nitrite are also formed due to the reaction of the ammonia and nitrogen oxides.

It will be noticed that residual oxygen is required in the stream in order to allow the second reaction to take place. This should be at least 1% v/v to allow the reaction to proceed to completion.

The use of selective catalytic reduction with ammonia has been known for around 40 years. More intensive development work has been undertaken in recent years in response to tighter regulatory requirements for NOx discharges, particularly with respect to combustion applications. This development work has resulted in improvement in catalyst effectiveness and robust, well-tried, processes are available from a range of competent suppliers. Of particular relevance to nitric acid manufacture is that SCR catalysts now offer:

- A life of greater than three years in normal conditions. In some cases a life of up to 12 years has been experienced.
- The ability to operate at lower temperature so that extensive re-heat is not required.
- Lower pressure drop units so that SCR can be retrofitted without sacrificing power recovery or affecting the balance of the plant energy network.

A range of metals (or their oxides) have been suggested, or used, as SCR catalysts including iron, chromium, vanadium, molybdenum and tungsten. These are used in conjunction with titanium dioxide, zeolite or alumina.

The process arrangement is shown in figure 3.4.

A small amount of ammonia slip of up to 10 mg/m^3 to atmosphere from the plant stack usually occurs although some suppliers offer a multi-catalyst bed arrangement. This allows the destruction of ammonia as well as NOx .

It should be noted, however, that the catalysts developed for the removal of NO and NO_2 do not remove N_2O. There is some indication that there may be an increase in N_2O release levels.

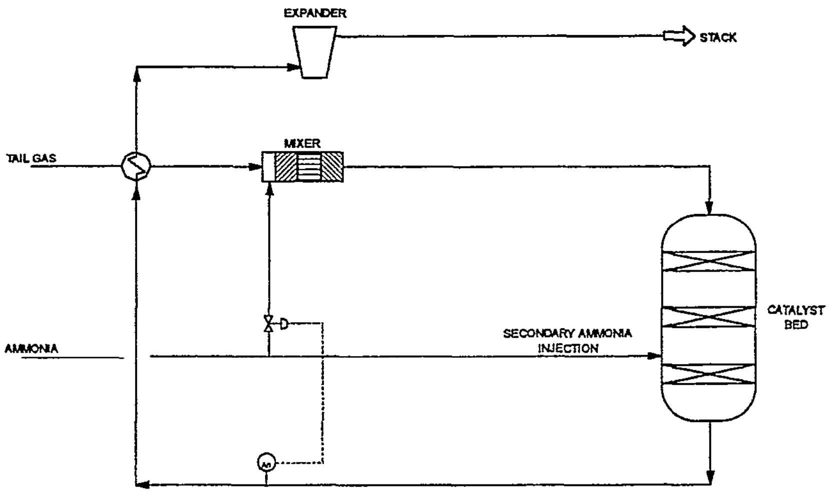

Figure 3.4 Outline of SCR flowsheet

3.3.4 Chemical Absorption (Scrubbing)

Chemical absorption techniques tend to be handicapped by the low solubility of NO in water. An effective absorption process has, therefore, to employ a mechanism whereby the NO is reacted rapidly within the liquid film adjacent to the gas. Absorbent liquids which have been used are:

Sulphuric Acid

Sulphuric acid of strength greater than 73% will react with equimolar mixtures of NO and NO_2 to produce nitrosylsulphuric acid (HSO_5N). The spent acid may be regenerated thermally for recycle.

Sodium Hydroxide or Sodium Carbonate

A mixture of sodium nitrite and sodium nitrate is formed. The process operates with around 50% removal and is at optimum effectiveness when the oxides of nitrogen are present in equimolar quantities. Nitrogen monoxide does not react with sodium hydroxide. This technique is capable of reducing a tail-gas concentration of 1200 mg/m^3 to 400 mg/m^3 as NO_2 when the operating pressure is in excess of 5.5 bara and the NO and NO_2 concentrations are almost equal..

The resulting sodium nitrite-nitrate solution from the neutralisation reaction is a liquid effluent and as such may present a disposal problem.

The alkaline absorption process should 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 in that sodium nitrate may freeze during the winter months.

Although present on existing processes, this abatement technique is unlikely on its own to be regarded as BAT.

Ammonia

Ammonium nitrate, which may be unstable, is produced. Whilst this tends to discourage the use of this absorbent, the decisive feature for using process depends on whether or not there is a demand for the ammonium nitrate produced.

Urea

Ammonium nitrate is produced. The same considerations apply as with the use of ammonia, except that urea is normally more expensive than ammonia.

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.

3.4 Review of Abatement Options and Plant Performance

3.4.1 General

The regulatory demands which have influenced the plant designs offered by the licensors of processes are:

1. USEPA requirement that NOx emission (expressed as NO_2) should not exceed 1.5 kg/tonne (as 100% HNO_3).

2. Requirement in many EU countries (based on TA Luft) that NOx concentration (expressed as NO_2) should not exceed 200 ppm (410 mg/m^3).

Typical values given for tail gas NOx concentrations from older plants without any emission control equipment vary between 1300 (2670 mg/m^3) to 2500 ppm (5140 mg/m^3).

More modern plant designs would produce between 600 (1230 mg/m^3) and 1000 ppm (2050 mg/m^3) NOx before control.

Typically, a modern plant will consume between 282-284 kg ammonia (stoichiometric 270 kg) and 50-160 mg catalyst, per tonne HNO_3 (expressed as 100%).

Of the ammonia loss, 3 kg/te is present in the tail gas as NO/NO_2, 3-4 kg probably as N_2O and the remainder as nitrogen.

3.4.2 Extended Absorption

This technique is now offered by licensors. Its use increases the capital cost of the plant as increased contacting capacity is required in conjunction with chilling equipment and recirculation equipment for coolant. It is only really an effective option for the higher absorption pressure processes.

Retrofit of extended absorption to existing plant is not really feasible and an increase in the design pressure of an existing plant is clearly impractical. Minor improvements might be achieved by the use of oxygen injection but this is more a method of allowing capacity increases without prejudicing emission limit compliance.

The achieved emission concentration levels of NOx are between 100 ppm (205 mg/m^3) and 200 ppm (410 mg/m^3). This undoubtedly reflects the imposition of a design criterion of 200 ppm rather than an ultimate limit. It has been observed that one licensor offers a combination of extended absorption in conjunction with selective catalytic reduction.

3.4.3 Non Selective Catalytic Reduction

Non selective catalytic reduction uses an auxiliary fuel to use up the residual oxygen and so create the reducing conditions. Perceived disadvantages of the process are the cost of fuel and the risk of carbon deposition on the catalyst which causes clogging. The system is also not available as an add-on system because of the need for a high temperature gas expander. The technique is used to a large extent currently in the UK.

3.4.4 Selective Catalytic Reduction

The advantage of selective catalytic reduction using ammonia over NSCR is the comparative ease with which it can be installed as abatement equipment on either new or existing plant. There is a negligible increase in tail gas temperature, which is beneficial for materials of construction. Also SCR systems are low pressure drop units which may be retrofitted with a minimal impact on the plant energy network and power recovery systems. Additionally, ammonia is always available on the plant. The technique is widely used. There are many reported examples of tail gas emission NOx concentrations of 150-200 ppm (310-410 mg/m^3). This may reflect the requirements of regulation rather than process capability, as there are no obvious barriers to achieving consistent results of 50-100 ppm (100-205 mg/m^3).

When retrofitting plant with SCR systems, however, the high integration of the existing plant has to be taken into account (see figure 3.3). This may make the retrofitting of units with SCR difficult, as it would require not only 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 re-configuring the train. Such changes are unlikely to be optimum.

Disadvantages of SCR include the possibility of ammonia slip through the bed and the requirement for stable operation of the plant to give stable temperatures at the bed inlet. There is also no reduction in Nitrous Oxide (N_2O) concentration across the system (see next section for comparison with NSCR).

3.4.5 Nitrous Oxide (N_2O) Treatment

It has been suggested that up to 6 kg of nitrous oxide per tonne of nitric acid may be emitted with the tail gas from a nitric acid process. Nitrous oxide in the atmosphere is relatively unreactive and little attention has been given so far to its treatment. It is however a potent greenhouse gas. SCR catalysts used for catalysts NO and NO_2 destruction do not reduce N_2O and there is some indication that N_2O level is increased by the SCR reaction.

In contrast NSCR catalysts have been shown to give in excess of 90% reduction of N_2O. In other words, similar removal to that experienced for NOx has been observed. Decisions, therefore, will have to be made as to which of these gases are more environmentally damaging and thus which route to take. It is expected that the first industrial applications of N_2O abatement will be on adipic acid tail gas streams.

3.4.6 Liquid Absorption Methods (Scrubbing)

In general terms, the absorption of NOx into a liquid only transfers the release from one medium to another.

For example, absorption into sodium hydroxide solution produces a mixture of sodium nitrite and nitrate. The effluent will require further treatment before it is discharged and the process only tends to find favour if sodium nitrate is being produced on site as a product. Even in these circumstances, extended contacting capacity is required, reducing the viability of the process.

There is also an associated operational problem since sodium nitrate has a tendency to freeze during the winter months.

It is also reported that the absorption rate into >73% sulphuric acid is twice that of an alkaline solution. As a result, the reduction of the nitrogen oxide content of a stream containing 1000 ppm (2050 mg/m^3) to less than 100 ppm (205 mg/m^3) is readily achievable. Extra plant equipment is required, however, to recover and reconcentrate the sulphuric acid and no commercial applications of the process have been identified.

3.4.7 Pressure Swing Adsorption

No commercial use of this process has been noted. The large capital cost and cyclic nature of the operation are obvious disincentives.

3.5 Costs of Abatement of Nitric Acid Plant

Costs of abatement of nitric acid plants are covered in Section 8, "Economics". The costs are expressed in terms of NO_2 recovered per tonne of daily installed capacity of nitric acid.

3.6 Concentrated Nitric Acid

3.6.1 General

Although the bulk of nitric acid production throughout the world is used directly as weak acid in fertilizer production, concentrated nitric acid is required for some uses, in particular, for the production of nitrated organic compounds and in the explosives industry.

Concentrated nitric acid is often manufactured using weak nitric acid as the feed material. The formation of the nitric acid/water azeotrope at a concentration of 68% HNO_3 precludes the use of simple distillation for concentration of the acid.

The methods in common commercial use are summarised below.

3.6.2 Extractive Distillation

96-98% concentrated sulphuric acid is used as a dehydration agent to break the azeotrope in a separate distillation column. The central part of the column achieves dehydration by mixing the nitric and sulphuric acid. The upper part of the column acts as a rectification section to concentrate the nitric acid. The lower part of the column acts as a stripping section to remove nitric acid from the dilute sulphuric acid before it leaves the column to be reconcentrated.

The use of magnesium nitrate as an agent for breaking the azeotrope has been reported but there are no readily available references to it in modern plants.

3.6.3 Direct Strong Acid Processes

These processes adopt the first steps of the process for the production of weak acid, but break the barrier of the azeotrope composition by compression and the direct absorption of NO_2 into nitric acid. After ammonia conversion, quenching and condensate separation, the vapour phase passes through two oxidising columns, in which NO is oxidized. The NO_2 formed is absorbed directly into nitric acid to form a higher concentration nitric acid.

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

Final concentration may be achieved by distillation in which the overhead product is concentrated nitric acid and the bottom product is 68% azeotropic acid.

A typical flowsheet is shown in figure 3.5.

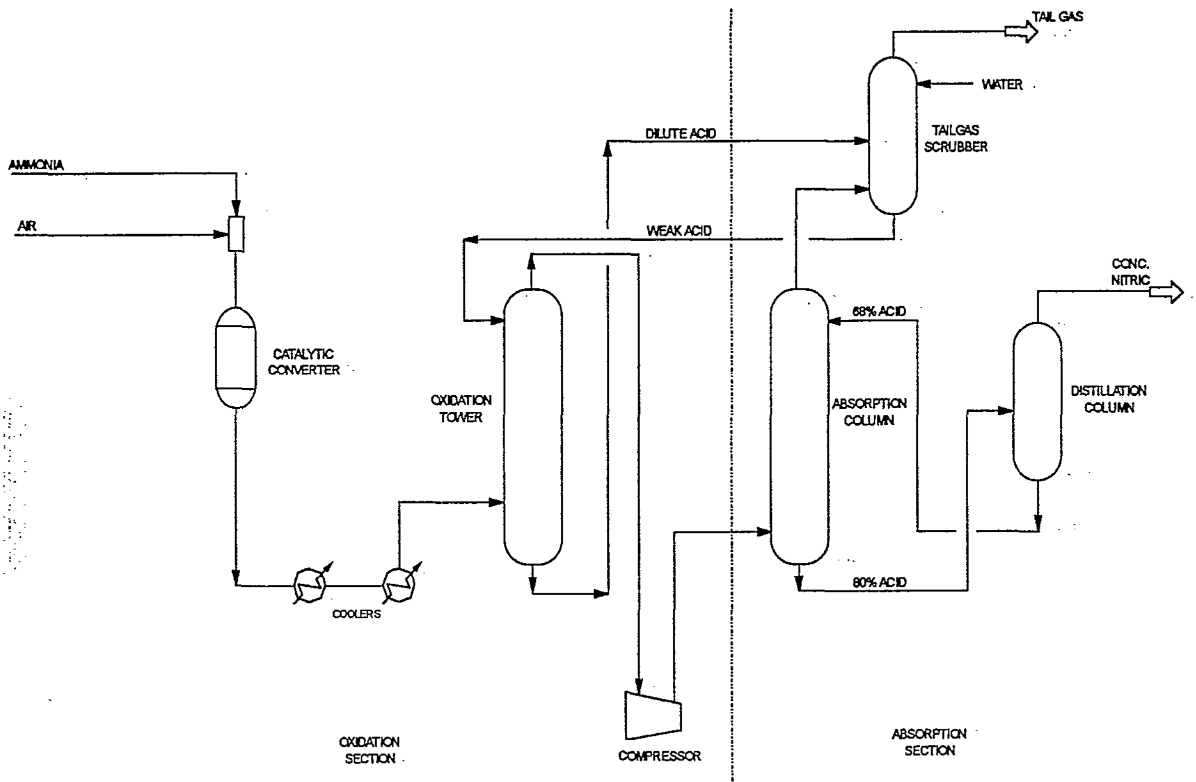

Figure 3.5 Simplified flow diagram : direct route concentrated nitric acid

The generation of emissions from the azeotropic distillation processes is low. The plants are usually operated as integral parts of weak nitric acid production. The non-condensable nitric oxides generated in the process are recycled to the weak acid absorption tower. The direct strong acid process produces gaseous emissions resulting from the discharge of nitrogen (ex oxidation air) from the weak acid absorption column. The release/abatement problem is therefore identical to that arising in weak acid plants and section 3.1.6 for should be referenced for abatement techniques and their effectiveness.

3.7 Nitric Acid Uses

3.7.1 General

The principal use of nitric acid is in the manufacture of fertilizers. The manufacturing process involves standard neutralisation, with little evolution of oxides of nitrogen in gaseous form. Other industrial uses result from the nature of nitric acid as:

a) A strong acid.
b) A powerful oxidising agent.
c) A nitrating agent in the organic chemical industry.

3.7.2 Metal Finishing

A number of metal brightening techniques are used to improve the surface finish of non ferrous metals and their alloys; some of these processes are electro-chemical and some are purely chemical. The steps in the process are usually:

a) cleaning and degreasing.
b) brightening.
c) anodising.
d) dyeing and sealing.

Nitric acid is frequently used in all of these stages. It is also sometimes used between steps to assist cleaning. Gaseous NOx is generated in all of the instances of nitric acid use.

3.7.3 Metal Pickling

Pickling is the process widely used for removing surface scale from stainless steel. The scale forms during hot working processes to produce sheet, plate, tube or wire. The scale is composed of metal oxides and it is removed by dissolution in acid, usually a mixture of nitric acid and hydrofluoric acid. The dissolution is accompanied by the evolution of nitrogen oxides.

3.7.4 Passivation

Nitric acid is sometimes used in conjunction with, or in preference to, electrical methods for the final treatment of the contact surfaces of process vessels for corrosive duties made in materials such as titanium. The oxidising effect of nitric acid forms a resistant oxide film on the surface of the metal.

3.7.5 Metal Dissolution

The dissolving of metals in nitric acid is the first processing step for a number of chemical processes, in particular in metal recovery processes. The re-processing of nuclear fuel is a typical example.

3.7.6 Nitration of Organic Compounds

The formation of nitro-organic compounds is an important transformation in the manufacture of many explosives and in the preparation of aromatic amines.

3.8 Releases During Nitric Acid Use

3.8.1 Gaseous Emissions

There is only a small release of nitrous fumes during the normal handling of weak nitric acid. Concentrated nitric acid can give rise to fumes at all times and handling equipment should be designed to avoid agitation and splash filling. All vessels should have back venting arrangements to avoid release during filling.

The greater part of the gaseous NOx emission occurs at the point of use. In the case of metal finishing and dissolving this is at the point at which metal is dissolved; in nitration processes within the nitration reactor. In all cases a mixture of NO and NO_2 is evolved, sometimes with traces of hydrogen, and in the case of organic nitrations, with volatile organic compounds.

Dry metal pretreatment of grinding, fettling or shotblasting generates dust.

3.8.2 Liquid Effluents

There are two main sources of effluents from metal processing activities. These are:

- The spent acid from the processing bath. This contains quantities of solid sludge and dissolved metal salts.
- The dilute acidic wash liquor from the metal wash area.

3.8.3 Solid Wastes

Solid wastes from nitric acid use comprise:

- Dry waste from precleaning operations such as shot blasting. The cleaner the metal is before acid treatment, the less the usage of acid during treatment.
- Wet sludge removed from the spent acid.
- Precipitated sludges formed as a result of treatment of the spent acid before discharge.

3.9 Abatement Techniques for Releases During the Use of Nitric Acid

3.9.1 Emission Sources

Releases of oxides of nitrogen resulting from the uses of nitric acid are similar in nature to those from the nitric acid manufacturing processes in that they consist largely of nitric oxide and nitrogen dioxide. The form of the emissions does, however, vary.

Metal Finishing and Pickling

Most metal finishing operations are performed in treatment baths at atmospheric pressure.

Access is provided for machinery to insert and remove metal from the bath. Gastight enclosures, therefore, are not practicable and scavenging air must be drawn through the space above the liquid.

The total releases are not high, with typical values are of the order of:

0.06-0.15 kg NO/ tonne steel processed.
0.10-0.28 kg NO/ tonne steel processed.

The flow is liable to fluctuate in rate and composition so that, without the application of abatement techniques, considerable local nuisance can be caused even when the total impact on the district air quality would be minimal.

Metal Dissolution

Many of the considerations in metal dissolution are similar to those associated with pickling. The composition and rate of off gas varies with the metal, the temperature, the form in which the metal is added to the liquid, and the rate at which additions are made. The system on the other hand is much more contained and the gases released are therefore more concentrated and amenable to control. Absorption in nitric acid which is subsequently used for dissolution is the favoured method and the use of oxygen injection to promote the oxidation and absorption of NO is widely used. As in the abatement systems for nitric acid plants, the use of chilling at the absorption stage can improve performance. The technique of adding peroxide solution to the process is an option that needs evaluation within the constraints of the requirements of the downstream processing steps.

For all of these processes the operator needs to demonstrate that the key operating parameters are identified and controlled. This is particularly important if the technology being used requires competences which are not normally expected within the operator's business.

3.9.2 Gaseous Effluents

Absorption (Scrubbing)

Absorption of NO and NO_2 into either alkali solutions or into nitric acid solution is complicated by the need to achieve reaction of NO to NO_2, either in the gas phase or the liquid phase, to achieve removal. The oxidation reaction of NO is very slow at low concentrations. The ratio of NO to NO_2 also influences the rates of reaction. Both factors also depend on a large number of other factors including:

- The nature of the metal being treated.
- The rate of travel of treated material through the bath.
- The temperature of the pickling bath.
- Composition of the pickling liquor.
- The residence time of extracted air in the pickling plant.
- Deterioration of the pickling liquor.

Three variations have been proposed to improve the effectiveness of absorption processes:

- The use of hydrogen peroxide solution.
- The use of direct oxygen injection.
- The use of potassium permanganate solution.

Addition of hydrogen peroxide to the absorbent solution increases the rate of oxidation of the NO and increases the overall efficiency of absorption. Advantage may be taken of the absorption effect of oxidising solutions on the gases evolved by adding hydrogen peroxide solution to the solutions in the bath. If oxidising conditions are maintained within the bath, nitrogen oxides release is reduced due to reabsorption.

Alternatively direct oxygen injection to the absorption column has the same effect as peroxide. It increases the oxidation rate of NO and enhances the overall rate of absorption, and is preferred to peroxide, where it is readily available.

Another alternative involves the addition of potassium permanganate to the strongly alkaline absorbent solution. This allows absorption of NO by a reduction action with the permanganate and a reconstitution of the permanganate solution by oxidation by NO_2. There is nevertheless a considerable consumption of material because the caustic and permanganate solution has to be discarded as soon as the alkalinity diminishes.

Selective Catalytic Reduction

Selective catalytic reduction using ammonia as the reductant may also be used. The installation is somewhat more complex than in a nitric acid plant because:

Gas flow is intermittent and flow rates fluctuate. Consequently the control systems for both heating and ammonia supply need to be extremely sensitive and reliable. Feed forward control will also be required.

Ammonia will often not be available on site. Auxiliary equipment to generate ammonia from urea might therefore be necessary.

3.9.3 Liquid Effluents

An improvement in the utilisation of acid in the processes is, in the first instance a management rather than a technological problem. Measures to reduce leakage, reduce drag out losses and to use countercurrent modes of metal rinse will in many cases reduce the total volume of waste required to be treated for disposal.

Developments in acid recovery techniques based on ion exchange or membrane techniques are unlikely to be applicable to small businesses.

3.9.4 Solid Wastes

Solid wastes from filtered spent acid, from precipitates from neutralised effluent waste and from air filtration systems after suitable dewatering are disposed of to licensed landfill.

4. PROCESSING ROUTES FOR HALOGENS/HALOGEN COMPOUNDS

4.1 Chlorine

4.1.1 Overview

Chlorine is manufactured on a large scale by the electrolysis of sodium chloride brine which is usually extracted from salt deposits. Potassium chloride brine may also be used although this process is much rarer. In the sodium chloride process, saturated brine is decomposed to hydrogen and chlorine gas electrolytically using a direct current. The overall reaction is represented as:

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

Hydrogen gas is normally evolved at the cathode (except as described below for the mercury cell process) and chlorine at the anode. Sodium hydroxide is produced as a co-product. There are three electrolytic processes that are used commercially:

- the mercury electrode process
- asbestos diaphragm process
- membrane process

The mercury cell and diaphragm processes were developed originally in the 1890s, in parallel. The subsequent development of the membrane process in the 1970s was primarily due to three factors:-

- increasing cost of power
- need to obtain higher purity caustic soda when compared with the diaphragm process
- increasing environmental concerns for asbestos and mercury

The first of these methods uses a flowing stream of mercury as the cathode. Sodium is released at the cathode instead of hydrogen due to its lower over potential on mercury when compared with other metal cathodes. The sodium reacts with the mercury to form an amalgam and is removed to a separate reactor, the denuder. Here the mercury is regenerated and recycled by reacting the amalgam with water in the presence of a catalyst. Co-products sodium hydroxide and hydrogen are also released and subsequently recovered..

In the diaphragm cell process, the anode and cathode are separated by an asbestos diaphragm. Chlorine and hydrogen are released within the separate compartments, but co-product sodium hydroxide, formed in the cathodic compartment, is free to mix with the original brine solution and is relatively impure. One advantage of the diaphragm process, when compared with the mercury process, is that it is able to operate effectively at lower brine concentrations. It is particularly suitable for solution mined brine.

The membrane cell is similar in structure to the diaphragm cell, but uses a cation permeable membrane to separate anode and cathode. The membrane allows, primarily, sodium ions and associated water to pass through into the cathodic compartment. The water is reduced to hydrogen, with the hydroxyl ions combining with sodium ions to produce caustic soda. This process therefore releases chlorine and hydrogen at the respective electrodes as before, but the caustic soda produced is of a much higher quality than that of the diaphragm process.

The diaphragm process is dominant in the USA, primarily due to the use of solution mining and the availability of low cost asbestos. Conversely, the mercury cell process is dominant in Europe, due to the ready availability of rock salt and mercury ores. The mercury process provided 95% of Japan's capacity in 1972, but was subsequently phased out completely by 1986. The change arose due to increasing concerns over mercury toxicity in Japan.

4.1.2 Overall Chlorine Process Description

The overall process is shown in figure 4.1.

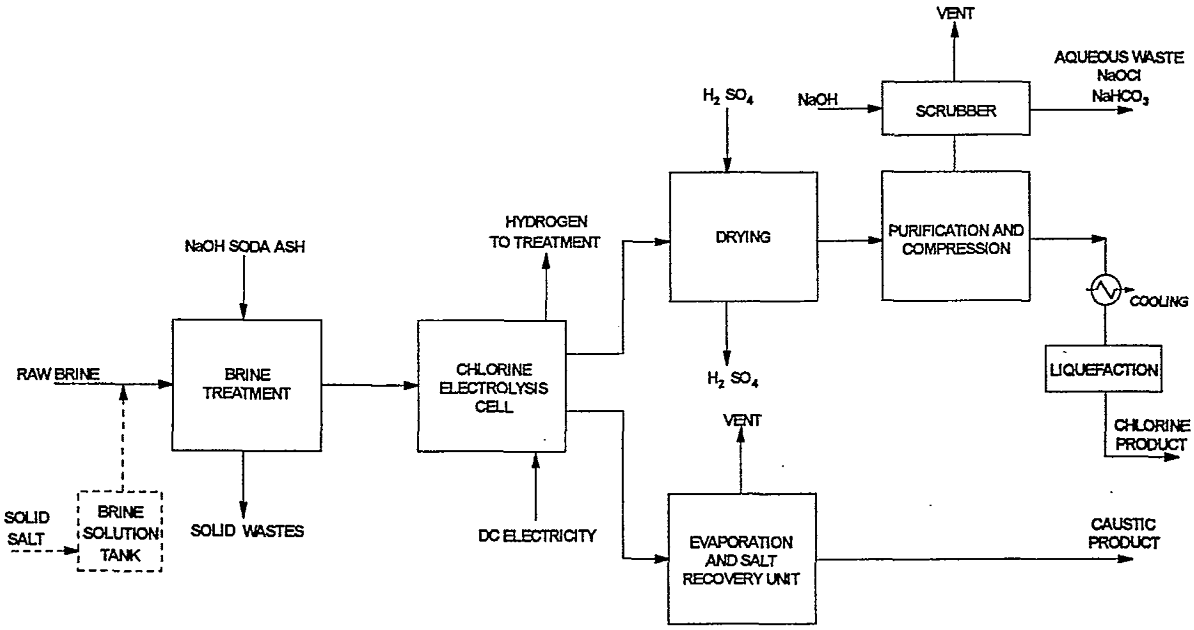

Figure 4.1 Chlorine Production Process

The basic raw material is usually solid salt, obtained from three primary sources; rock salt, solar salt and vacuum evaporated salt from solution mined brine. In USA and Europe rock salt is the most common feedstock. It is generally purer than solar salt, but will still require further purification. The solid salt is dissolved in a hot circulating solution of spent brine and make-up water. Modern re-saturators are closed systems, but open pits have also been used. The depleted brine is normally de-chlorinated prior to re-saturation. De-chlorination is particularly required for mercury cell and membrane processes to prevent mercury chloride formation in the mercury cell, or damage to the membrane, respectively. De-chlorination may be achieved by acidification with hydrochloric acid.

The brine solution is then treated to remove the impurities such as calcium and magnesium. Treatment involves the addition of sodium carbonate solution, followed by sodium hydroxide, to precipitate calcium carbonate and magnesium hydroxide. The resultant suspension is allowed to settle in clarifiers, and then filtered in sand or diatomaceous earth beds,. Traces of heavy metals will also be removed in these stages. The extent of purification depends on which type of electrolytic process is used.

The membrane process requires the most extensive brine pre-treatment to prevent premature blocking of the membrane and provide a reasonable life expectancy. The diaphragm process requires the least level of purification. Typically, the membrane processes require impurities to be reduced to ppb levels eg: divalent calcium and magnesium ions, harmful to the cation membrane should be reduced to less than 50 ppb. A final cation exchange purification step is therefore needed. Heavy metals removal is important for the mercury process to prevent hydrogen formation within the cell.

The method and extent of pre-treatment are dependent on the nature of impurities in the raw brine/rock salt. Iodine, aluminium, silica all have adverse effects on membrane performance and require tertiary treatment with anion exchange resins.

The brine purification "muds" are normally washed to remove residual soluble materials including sodium chloride, before disposal as a solid waste.

Electrolysis

In the chlor-alkali process there is a major power requirement and electricity supply should be seen as the equivalent of a raw material. The direct current is supplied through silicon diode rectifiers, or thyristor converters (more modern plants). In supplying the power, the cell current requires to be constant even where the voltage is varying due to cell operating conditions and cell availability. Cell rooms have multiple banks of cells to meet the throughput requirements of the chlor-alkali plant. Economies of scale with respect to power supply result when a large number of high amperage cells are connected in series, with feeder dc voltages in the range of 200 to 400 volts.

The brine is then electrolysed to generate the main products of chlorine and caustic soda. In modern plants the anode is generally titanium, coated with ruthenium and titanium dioxides, to give a purer chlorine product. Acidification of the brine to pH < 6 prolongs the life of the coating and reduces the formation of hypochlorite/ chlorate in the brine. The specific electrolytic process is described more fully in subsequent sections, which cover the mercury cell, diaphragm and membrane processes, respectively. However it should be noted that the mercury process requires the highest electrical energy for chlorine generation and the membrane process the least. Typically cell voltages range from 2.8v to 5v, and current densities from 2 to 10 kA/m^2, dependent on the process. The mercury cell process however requires no steam heating (for evaporation) to produce a suitable caustic soda product.

Table 4.1 provides a simplified comparison of the three processes.

Table 4.1: Comparison of cell requirements for mercury, diaphragm and membrane cells (source Kirk Othmer, vol 1).

Requirement	Mercury Cell	Diaphragm Cell	Membrane Cell
anode	metal oxides (1) on titanium	metal oxides (2) on titanium substrate	metal oxides (2) on titanium substrate
cathode	mercury on steel	steel or steel coated with activated nickel coating	steel or nickel with catalyst nickel coating
cathode product	amalgam	10-12% NaOH, H_2 plus depleted brine (15-17%)	30-33% NaOH, H_2, < 0.01% NaCl
decomposer	50% caustic and H_2		
caustic after evaporation	50% (no evaporation)	ca 50% , contains ca 1% salt	ca 50% , low salt (< 0.01%)
steam	none	1500+ kg/t NaOH	450+ kg/t NaOH
Voltage	4-5	3-4	2.8-3.3
current density (kA/m^2)	7 - 10	0.5 - 3	2 - 5

(1) - typically ruthenium and titanium dioxide mix

(2) -ruthenium dioxide

Product Recovery

Chlorine recovery involves cooling, drying (usually with dilute sulphuric acid), purification to remove chlorinated hydrocarbons and finally compression/ liquefaction for storage (where chlorine is sold in liquid form). Chlorine liquefaction is typically a two stage process. CO_2 is used as the refrigerant in the first stage to liquefy about 80% of the chlorine, followed by a second stage process using chlorofluorocarbon (CFC) to refrigerate about 15% of the remainder. The residual 5% of the chlorine may be reacted with caustic soda to form sodium hypochlorite solution. Inert gases that would otherwise build up are vented after the refrigeration stage. CO_2 and CFCs are harmful pollutants and they may find their way into the atmosphere by escaping through refrigerant compressor seals

The caustic soda is generally concentrated by evaporation to the required product strength and stored. The extent to which this is required is dependent on the electrolytic process. The mercury cell process generates a purer, more concentrated caustic soda than either of the other cells.

Hydrogen may be treated as a co-product, as it is normally of high purity (>99%). Recovery involves cooling, scrubbing, compression and sold or used to make other products downstream eg hydrogen chloride. Alternatively it will be vented/ flared, dependent on plant configuration, and demand.

Emergency venting

Large scale releases in the cell room are unlikely, as production of chlorine ceases as soon as the power supply is shut-off. There is possibility of large releases from other chlorine handling sections of the plant. It is therefore normal practice to provide for emergency relief of the chlorine. The 'emergency absorption plant' is designed to absorb excess chlorine that may be emitted from emergency relief valves. The vented chlorine is absorbed into packed columns of sodium hydroxide to produce a chlorinated caustic solution, which may be used subsequently to make sodium hypochlorite. Residual vent gases, containing less than 10 mg/m^3 of chlorine, are normally vented through elevated stacks.

Releases and Pollution Abatement

Whilst mercury and asbestos are correctly considered as having major pollution potential, it is important to recognise that major issues for the chlor-alkali industry include:-

- chlorine emissions and spillages.
- treatment of caustic soda, sodium hypochlorite streams, where required.
- emergency venting of chlorine, as discussed above.

This section describes the releases to air, water and land that may occur in chlorine processing and identifies the primary abatement techniques required to minimise such releases. These include chlorine, caustic, hypochlorite and acid streams. More specific treatment of the special wastes arising from the mercury cell and diaphragm processes are addressed within sections 4.1.2 and 4.1.3.

Releases to Air

The primary releases to air are likely to be chlorine and hydrogen, although there is a risk of air-borne sodium chloride from open pit type of brine re-saturator.

Chlorine releases may arise from:-

- the non-condensable gases in the compression/ refrigeration loop.
- storage tank vents.
- venting arrangements from tanker loading/ unloading operations.

These vents, tail gas from liquefaction, air streams from brine de-chlorination, or maintenance purging etc should be manifolded to minimise the number of discharge points that enter the atmosphere, after chlorine is removed by absorption. A two stage caustic scrubbing system may be used. The hypochlorite generated by the caustic scrubbing may be regarded as a co-product, or handled as a waste stream. It may be practicable to recover chlorine from the hypochlorite by acidification. The absorption system is normally sized for emergency venting (see earlier).

Until recently, chilled carbon tetrachloride had been used in some processes in the UK to remove residual chlorine from the vent gases. Chlorine is then recovered by stripping. The use of carbon tetrachloride creates its own environmental concerns with respect to formation of a range of chlorinated hydrocarbons and is itself a prescribed substance.

Consequently emphasis has been placed on using other methods of chlorine removal from the vent gases. In particular, caustic scrubbing is very effective at removing chlorine and produces a useful by-product, sodium hypochlorite, at the same time. This removal process should be regarded as BPEO.

Using best available caustic scrubbing, control and monitoring technology it should be practicable to reduce the chlorine discharge concentration in the vents to less than 10 mg/m^3 even during emergency venting and significantly lower under normal conditions. Final gas streams should be vented at a safe height, typically 30-40m.

Unsold, or unutilised hydrogen, is normally vented, although BAT would favour maximum utilisation as co-product or fuel. There is no specific release limit for hydrogen as it is essentially non-polluting. Releases, however require control for safety/operational reasons, particularly for chlorine/ hydrogen contaminated streams. Here limits of typically 2% hydrogen are set to avoid explosive mixtures.

Releases to Water

Potential releases to water include purge brine streams, hypochlorite solutions from the caustic scrubbing processes, spent sulphuric acid from chlorine drying, weak caustic and brine streams from evaporators and washdowns. Water run-off, particularly from the process areas are also likely to be contaminated and will require treatment before discharge. Where it is not practicable to use all of hypochlorite as a product, excess hypochlorite requires disposal.

Essentially conventional effluent treatment plant (see also chapter 6) may be used to minimise the various effluents releases to water courses. The various acid and alkaline effluents can be used to balance discharges.

Improvements have been made in the treatment of waste sodium hypochlorite and chlorinated caustic in recent years using catalytic destruction (ref. Mod Chlor-alkali Tech - Vol. 6). A heterogeneous supported nickel catalyst may be used to decompose the sodium hypochlorite into brine and oxygen gas; reducing an effluent stream of say 15% hypochlorite to typically 1 ppm in a single pass.

Releases to land

Brine purification wastes are produced, but provided they are not contaminated with hazardous material and may be disposed of to non hazardous landfill (calcium and magnesium salts primarily).

Spent filter elements also require landfill. Again this is non hazardous except where contaminated with mercury or asbestos (see sections 4.1.2 and 4.1.3).

Releases from Refrigerants

The selection of refrigerant to chill and liquefy chlorine gas has significant environmental implications. Refrigerants with significant ozone depletion potential such as CFCs are being replaced with non-ozone depleting refrigerants such as propane/butane mixtures. “Transition” refrigerants such as HCFCs should also be replaced in the longer term.

Refrigerants which 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
- health and safety

Other Releases

Other releases that will arise from the chlorine process will include transformer and rectifier oils which should only be disposed of by recycling to the original supplier or a qualified recycling company.

4.1.3 The Mercury Cell Process.

Process description

An arrangement for the Mercury cell is given in figure 4.2. Mercury flows down the inclined base of the cell and forms the cathode. The hot saturated brine flows co-currently on top of the mercury. Anodes are suspended in the flowing brine solution with only a small gap between them and the mercury covered cathode. Sodium is released at the cathode, forming an amalgam with the mercury. This amalgam is maintained at a low concentration in order to retain good flow characteristics. A small underflow weir is provided at the downstream end of the cell to maintain a mercury layer within the cell. This arrangement is designed to avoid exposing the metal of the cell floor, thus preventing evolution of hydrogen, which has a lower overpotential on steel or other heavy metals. This type of design minimises the risk of an explosive mixture forming between the hydrogen and the chlorine. As stated earlier, removal of heavy metals during brine treatments is also essential.

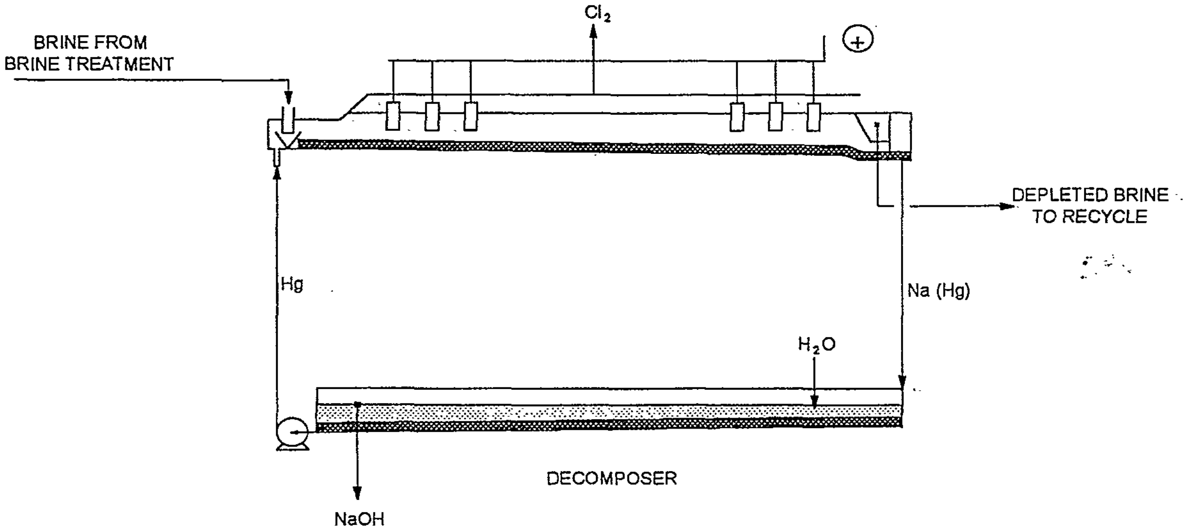

Figure 4.2: Simplified mercury cell process.

Chlorine leaves from the top of the cell through the chlorine header out of the cell. The depleted brine passes over the over-flow weir and is recycled to the brine make-up tank for re-saturation.

The sodium amalgam/ mercury layer enters a separate reactor, known as the denuder, where it is reacted with demineralised water in the presence of a graphite catalyst activated by iron, nickel or cobalt oxide. At this stage hydrogen gas and sodium hydroxide solution are produced, and the mercury recovered. The mercury is then recycled to the electrolysis cell.

The problem with the mercury cell process is that all products, waste streams and equipment are likely to become contaminated with highly toxic mercury. Extensive steps to abate mercury as the main pollutant and to minimise the quantities of mercury released through gas and liquid effluent streams to the environment are required.

Control of Releases from the Mercury Cell Process

Legislation

The mercury cell process causes most concern from the perspective of environmental impact. Mercury, and chemicals derived from, or contaminated with it, are extremely toxic even in very small amounts, whether released into the air, water, or landfill. Due to the environmental concerns, there has been increasing inter-governmental legislation and increasing pressure to phase out mercury cells, with the intention of switching to other cell types (particularly the membrane cell).

The control of mercury to the environment is covered by the EC Black List and the UK Red List. Operators are required to reduce the level of discharge of mercury to water to below $5\mu g$/litre. The European Union (EC) has also compiled regulations for the best available techniques for pollution abatement in chemical industries. The European Integrated Pollution Prevention and Control (IPPC) Bureau commenced studies into BAT for the chlorine process in 1998, in order to produce and publish information to the national regulatory bodies and European industry. These BAT regulations are required to be put in effect, within seven years (2005) and cover releases to air, water and land.

In the US, the Environmental Protection Agency (EPA) has specified methods for controlling aqueous wastes containing mercury in a document defining Best Demonstrable Available Technology (BDAT). Target levels of $30\mu g/l$ for mercury in the waste water after treatment have been set. Additionally, the level of mercury in the separated solids filter cake should be categorised into high and low concentrations using a cut-off of 260 mg Hg/ kg cake. Requirements for treatment of the highly contaminated waste are specified.

Achieved Releases

Mercury cell operators have made significant strides in recent years to reduce mercury releases by improvements to both processes and pollution abatement technology. Based on such achievements, Euro Chlor, which represents chlorine producers in Europe, has stated a case for retaining the mercury based process . In a paper, entitled 'Chlor-Alkali Mercury Cells: Economics and the Environment' (October 1994), Euro Chlor has assessed total mercury emissions from chlor-alkali plant within the perspective of natural sources of mercury, such as geysers and hot springs, mineral ores and seawater, and releases from other industrial processes.

Euro Chlor reported that, for 1993, mercury releases form the European chlorine industry amount to 19 tonnes of the estimated worldwide total of 20,000 tonnes (0.095%). Since the late seventies when the gravity of the toxic effects of mercury were first realised, the emissions per tonne of chlorine produced have been reduced by approximately 90%. This has been made possible by considerable investment in pollution abatement technology by the chlor-alkali industry. Total European emissions could be reduced by a further 30%, to 13 tonnes per year, if all the existing European chlor-alkali plants were to be equipped with this same mercury pollution abatement technology. New technology achieving even further reductions by 2010 is likely. The chlor-alkali industry produces very low levels of mercury when compared with ore smelting and the combustion of fossil fuels.

Additionally, it has been estimated that mercury releases for the European chlor-alkali industry should be less than 1.9 g/tonne of chlorine by the year 2010, compared with the 1993 figure of 2.8 g/te Cl_2. This forecast figure would represent less than 0.2% of the anthropogenic global mercury releases to air and water. The trend represents a combination of :-

- plant closures.
- selective plant conversions to alternative technologies (eg membrane process).
- improvement to mercury containment by appropriate capital investment.

The mercury process remains viable due to the extent of pre-existing capacity. It is likely that, if and when new chlor-alkali capacity is required, the membrane process will be more economic. Japanese industry no longer uses the mercury cell process and all new developments are based on the membrane process. Similarly, in the USA no new mercury based process have been built since 1969 and since 1983 all new investment has been in the membrane process.

From the above trends, the chlor-alkali industry considers that there is no basis for specifically phasing out existing mercury cell chlorine facilities by the year 2010. The required investment to upgrade current plants (ca £200m) would be more effective if used in industries that release much greater amounts of this toxic metal. It should be noted that the European chlor-alkali industry constitutes about a quarter of the world wide production of chlorine.

Best available technology for abatement of mercury

Section 4.1.2 identifies the major sources of releases to the environment and methods for their abatement. Potentially all of these streams and the products may become contaminated with mercury and specific abatement treatment is necessary to reduce mercury contamination. BAT for minimising mercury releases to air, water and land is described in this section.

Releases to Air

The hot moist chlorine from the cells will contain small amounts of mercuric chloride, due to reaction with mercury. Most of the mercuric chloride will be removed completely in the subsequent processing (cooling and compression process) and is fed back into the brine with the condensate. The chlorine gas stream entering the refrigeration units contains small quantities of 'non-condensibles', primarily as a result of air in-leakage at the cells. The venting of these inerts may cause trace amounts of mercury to enter the atmosphere.

Wash operations performed on the mercury during its entrance to, and exit from, the cell result in the production of a 'weak' hydrogen stream. This stream, which is diluted with air to keep it below the explosive limits, contains mercury. Abatement involves reaction with chlorine in a packed reactor, when mercurous chloride (Hg_2Cl_2) is deposited. This is then washed with chlorinated waste brine producing a [$HgCl_4$] complex, which is recycled to the cells. The complex breaks down to mercury and chlorine during electrolysis. The cleaned gas, containing traces of mercury and air, is normally vented to atmosphere.

Mercury levels in the cell rooms are controlled to ensure a safe working atmosphere in the cell room itself and to reduce the amounts of mercury released to atmosphere through the cell room ventilation system. Background levels of mercury in the cell room arise chiefly from spillages of mercury which impregnate floor tiles and other building fabrics. The more obvious methods for reducing this hazard are careful transport of mercury and improved house keeping, including the sweeping or vacuuming of the smallest traces of spilt mercury. The use of impervious flooring in the cell rooms constitutes BAT. For example floors may be constructed of smooth hard tiles sealed with resin to avoid gaps or crevices.

Cell maintenance could result in a release of mercury vapour to the atmosphere. Effective operating and maintenance procedures are essential and include:-

- covering by a layer of plastic or water, at all times, during maintenance to inhibit fugitive release of vapour.
- regular checking of mercury pump glands and seals to ensure their integrity.
- scheduled maintenance of the cells to minimise need for de-contamination and to maximise effectiveness of maintenance.

Reduction in emissions to the air may also be achieved by changes of cell configurations, such as use of steeper bases to reduce depth of mercury film and vertical decomposers to minimise volume of mercury. These changes assist in reducing the quantity of Hg required and its vaporisation.

From a typical mercury cell plant many of the emissions to air arise from tank breather valves and various unit operations integral to the refining and recycling stages of the process. BAT for mercury removal from such gas streams and from hydrogen streams includes using oxidising scrubber liquors eg hypochlorite and chlorinated brine. These techniques are much more effective than the use of refrigeration alone.

Releases to Water

The spent brine is largely re-cycled but, to avoid accumulation of contaminants, a spent brine purge is required. Unless treated, the mercury will remain dissolved in the brine even if it becomes alkaline, whilst the chlorine concentration remains low. Purge streams from the spent brine, waste sodium hypochlorite, aqueous/ caustic scrubbing liquors and process area drainage should be treated to minimise mercury releases before discharge to water courses.

Facilities within effluent treatment plants should be designed to remove and recover mercury form all aqueous streams, as well as the normal chlorine related emissions (see section 4.1.2).

Treatment with sodium bisulphide is used to remove residual chlorine and to form a mercuric sulphate compound, which precipitates out from the solution. The mercury contaminated solid is separated by filtration and the essentially mercury-free waste water is then discharged. The solid waste is handled as described below. Other recommended methods for removal of mercury include:-

- A reduction technique with sodium borohydride $NaBH_4$.
- the use of specific ion exchange resins.

The treated aqueous effluent is normally discharged under consent into a nearby water course.

Releases to Land

Historically, spent contaminated filter medium has been discharged as a hazardous waste to authorized landfill sites. The spent nickel catalyst may be recycled by specialist vendors or discharged to hazardous waste landfills, dependent on nickel price. Similarly, brine purification wastes contaminated with mercuric chloride have been disposed of to hazardous waste sites.

There are however improved techniques for maximising recovery of mercury from solid wastes. Euro Chlor has proposed a range of techniques for treating solid wastes contaminated with mercury. It recommends the following methods as providing BAT:-

- Mechanical/physical treatment, such as brushing, ultrasonic vibration, vacuum cleaning and nitrogen freezing (for rubber coated steel).

- Water treatment in closed washing machines or with high pressure jets for the removal of attached mercury.

- Chemical treatment with hypochlorite, chlorinated brine or solutions of hydrogen peroxide. Dissolved mercury may be recirculated in the brine stream or recovered in water treatment.

- Distillation of mercury from solid waste (mercury boiling point is 357°C at normal pressure) carried out in special distillation units. Special attention should be given to treatment of the exhaust gases from these and other installations. Some solid wastes however, cannot be distilled.

Similar methods are recommended in the USA, where the EPA has specified a method for the treatment of solid (semi-solid) waste that involves precipitation by sulphide and hydrazine, during waste water treatment. The waste is composed of water and diatomaceous earth filter aid. The EPA recommends that the highly contaminated waste (greater than 260gm Hg/ kg solid) is treated by roasting and retorting. Dilution of the overall mercury concentration to less than 260 mg Hg/kg is not acceptable.

Low concentration waste is treated by acid leaching followed by sulphide chemical precipitation.

Removal of Mercury from Products

Some of the mercury is lost in the chlorine, caustic soda, hydrogen and related chlor-alkali products. This mercury would eventually be released to the environment at point of use. Customers for chlor-alkali products have in recent years encouraged mercury removal at source, by demanding tighter product specifications.

The mercury contamination of the NaOH product may be reduced to less than 50 ppb using pressurised plate filters impregnated with an activated carbon coating. The spent filter medium is handled as a solid waste. Alternatively graphite candle filters or carbon impregnated filters may be used.

Hydrogen generated in the decomposer or denuder cell is termed 'strong hydrogen' and is the main source of hydrogen as a product. It is contaminated with mercury vapour entrained in the hydrogen stream. Primary removal of mercury is achieved by cooling, followed by scrubbing with sodium chloride, sodium hypochlorite and sodium bicarbonate in packed towers. Mercurous chloride is produced and removed from the scrubber liquor in the effluent treatment plant.

Adsorption on activated carbon is also a suitable technique for final polishing. Mercury levels may be reduced to less than $10\mu g/m^3$ by such combined methods. The mercury may be recovered from the activated carbon using specialist recyclers to regenerate the activated carbon. A potential source of atmospheric emission is waste unsold hydrogen released to the air, hence mercury removal is essential.

Dry chlorine product contains negligible levels of mercury and no specific treatment is required. Mercury contamination of the hypochlorite originates from the sodium hydroxide used to produce the hypochlorite. Improving the quality of the caustic, by de-mercurisation, will minimise mercury levels.

In Europe, a target figure of mercury releases to all media of 1.9g Hg/tonne chlorine produced has been established. Use of the techniques outlined above are essential to meet this target. Additionally, accurate monitoring of the ambient mercury concentrations is also essential.

The above recommendations for the chlor-alkali industry are subject ongoing review but are due to become effective in Europe from the year 2005 onwards.

4.1.4 Diaphragm Cell

Figure 4.3 provides an illustration of the basic cell.

Process Summary

Purified brine flows into the anolyte compartment and then through the diaphragm into the catholyte section. There is no separation between the caustic, which forms at the cathode and the spent brine. Side reactions result in products such as sodium hypochlorite and sodium chlorite, which also remain in the brine/caustic mixture. Hydrogen is evolved at the cathode and kept separate from the chlorine by the diaphragm.

Chlorine is formed at the anode and contains impurities such as carbon dioxide, oxygen, and some hydrogen. Recovery and treatment is as described in Section 4.1.2. The caustic/brine solution is partially evaporated, precipitating much of the unreacted sodium chloride. This solution is then filtered, the brine recirculated and the caustic soda evaporated further still to yield solid products.

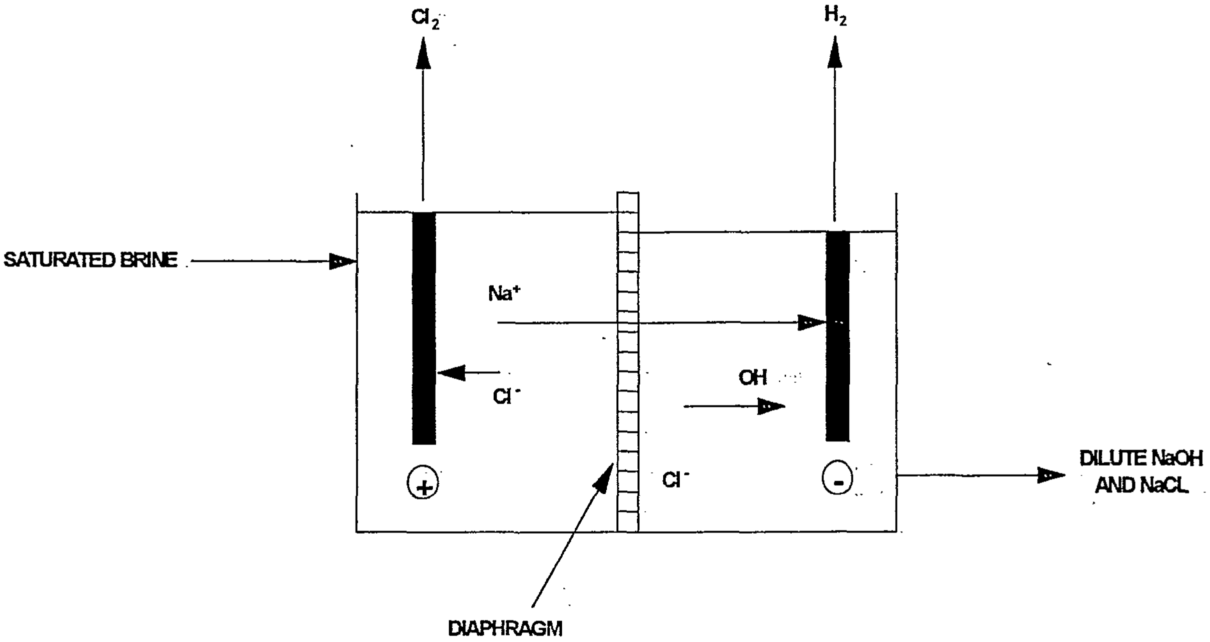

Figure 4.3: Simplified diaphragm cell

The diaphragm is commonly made of an asbestos based material, the purpose of which is to keep the liberated chlorine and the hydrogen and alkali hydroxide separated, thereby greatly improving the efficiency and avoiding the risk of hyrogen-chlorine explosions. Asbestos was selected originally as the material for the diaphragm due to its physical and chemical stability. It is also an abundant raw material and inexpensive.

Developments in diaphragm technology have been oriented towards improving performance and service life. Recent improvements include modified asbestos diaphragms, which rely on polymers such as fibrous polytetrafluorethylene to provide a porous substrate. The modified diaphragms have reduced cell voltage and permit the use of dimensionally stable anodes e.g.

comprising metal oxides/titanium substrate. To maintain the hydrophillic nature of the diaphragm, sodium carbonate may be introduced. Non-asbestos diaphragms have also been developed and used commercially. These comprise chemically resistant polymeric materials such as microporous polytetrafluoroethylene modified with sodium carbonate or polymethylmethacrylate, which has improved hydrophillic properties.

Best available technology for the diaphragm cell process

Introduction

Apart from the normal range of pollution abatement required for chlor-alkali processes, the diaphragm cell processes introduces another polluting material, asbestos. Asbestos fibre, is carcinogenic; creating specific environmental concerns. The best practicable environmental option would be represented by the use of diaphragms constructed of materials which do not contain asbestos. The developments described above, therefore represent BPEO. BAT for asbestos diaphragms requires effective controls on handling and disposal of asbestos.

Releases to Air

Releases to air of primary concern are chlorine and asbestos. The abatement of chlorine releases is described in section 4.1.2.

The Control of Asbestos in Air regulations of 1990 provides legislation to limit emissions of asbestos to less than 0.1 mg/m^3. Emissions must be monitored at intervals of not less that six months and operators have a duty to try and prevent emissions to the atmosphere on the grounds that it is a known carcinogen. UK legislation also set out guidelines for safe working practices.

Strict precautions for handling asbestos are therefore essential to avoid release of asbestos dust. Typically the asbestos used on the plant is brought in sealed containers which are opened in a vacuum and subsequently vented to atmosphere via a suitable filter.

Releases to Land

Typically between 1 and 2% of the diaphragm cells, should be replaced, continuously, due to their relatively short life. The diaphragms must be removed from their cathode mesh support using for example a water lance, then double bagged, and disposed of in a specialised landfill.

4.1.5 Membrane Cell

A typical membrane cell is shown in figure 4.4. The membrane cell was developed by the chlor-alkali industry, in response to the demands for decreasing energy consumption and pollution emissions from their processes. 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. The brine introduced to this process, as in the diaphragm cell, is purified by precipitation, filtration and ion exchange to prolong the life of the membrane. Sodium carbonate is generally used

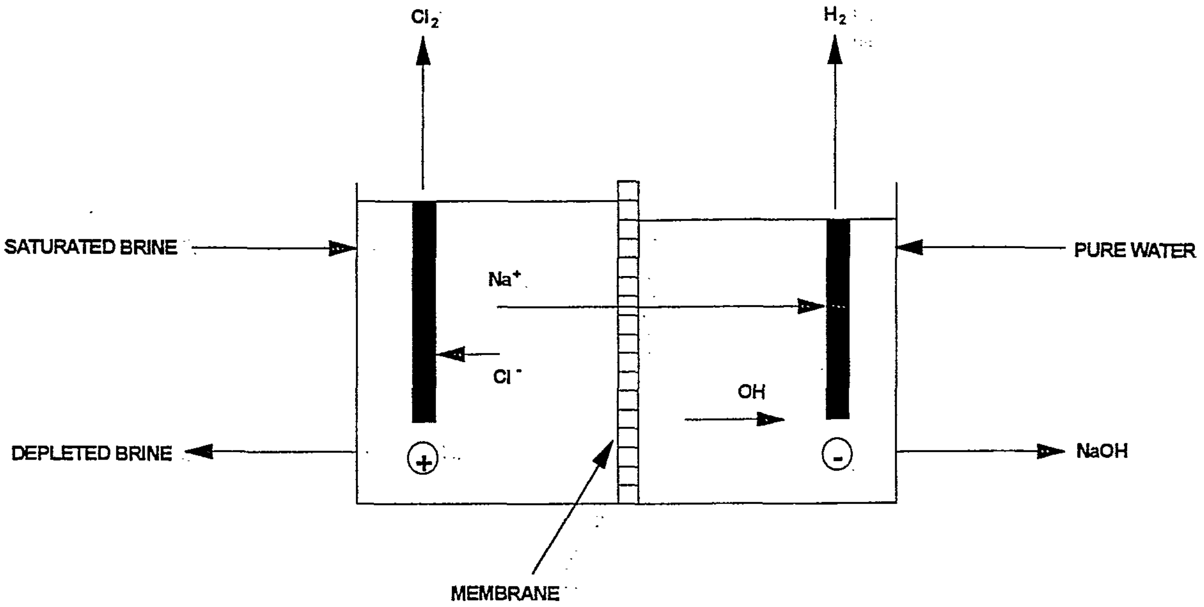

Figure 4.4: Simplified membrane cell

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

The purified brine enters the anolyte compartment and spent brine is removed from the same compartment to maintain a minimum chloride concentration. There is no significant transport of chloride in through the membrane into the catholyte. Water is electrolysed at the cathode and requires make-up to maintain the cell reaction. The water addition rate needs careful control to avoid production of too dilute a caustic product. In some processes the water stream is introduced into a recirculating caustic stream, which is then fed to the catholyte compartment.

The ideal membrane provides for:

- high selectivity for Na^+ transport
- no anion transport, particularly Cl^-, ClO^-, Cl_3^-
- zero reverse migration of OH^-
- low resistivity
- good mechanical properties and long term stability

Membrane construction is specialised and tends to be limited to very few companies. Recent developments include the production of laminated membranes to achieve the optimum balance of properties (see below).

The cation permeable membrane allows water and sodium cations to pass through it. Hydrogen and chlorine are again produced and the resulting sodium hydroxide solution is very high purity due to the efficiency of the membrane. The caustic is, however, relatively low strength and must be concentrated in a subsequent process. The chlorine depleted brine is recirculated and extra salt added for re-saturation. The chlorine gas produced is not as pure as that produced by the mercury process and contains oxygen, which has to be removed by liquefaction and evaporation. The chlorine produced also 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 have shorter lives.

This process consumes 25% less energy than the mercury cell process. Due to the temperatures reached in some areas of the plant, some of the materials of construction have to be of special heat, and corrosion resistant quality.

A leading Japanese producer of chlorine and caustic soda has invested resources in membrane cell technology, since the membrane process is recognised to be the most energy saving method. The company pioneered the development of a per fluoro-carboxylate membrane material. In 1982, the company developed a system comprising a high performance membrane with hydrophilic surface. The system also operated, in effect, as a zero gap cell with a hydrogen over voltage of only 0.1V. A Raney Nickel catalyst was used.

The membrane cell may be used to retrofit diaphragm cells; reducing energy consumption to below 2400 dc kWh/t of NaOH. The membrane cell may also be used to convert mercury cell processes. One Japanese plant, which under went this conversion reduced its energy consumption by 1000 dc kWh/t of NaOH produced and also saved one third of the floor space (due to the compact design of the membrane cells). These cells are capable of producing 35% caustic soda with a very low salt content of only 15 ppm.

One of the main concerns in the use of membrane technology is the life span of the actual membrane, and the length of time that it would be able to operate above a certain level of electrolytic performance. One factor, leading to the eventual degradation of membranes, involves the stagnation of chlorine bubbles in contact with the membrane at the brine level. This causes the precipitation of sodium chloride inside the membrane, giving rise to blistering and weakening. Also, despite mechanical strengthening, membranes are damaged by the vibrations caused by pressure fluctuations within the cell. Modern membrane materials are typically constructed in layers, which may comprise:

- a sulphonic and/or carboxylic group polymer i.e. to provide for Na^+ transport.
- polytetrafluoroethylene or polyester fabric to provide support.
- specialist coatings to improve performance.

In summary, membrane cells produce high quality caustic soda with a very low salt content, whilst requiring less energy and, typically, two thirds the floor space of contemporary mercury cells. The caustic produced requires less steam for concentration and hence less power consumption when compared with the diaphragm cell.. The membranes do however have to suit the particular application. There is a trade off between mechanical strength and caustic quality. Also, each actual membrane cell has typically, only the production capacity of three quarters of a mercury cell.

Sources of Releases for the Membrane Cell Process

The membrane cell process appears to have a distinct advantage from an emissions viewpoint in that it contains neither mercury nor asbestos. The primary releases to air, water and land are as described in section 4.1.2 and the same abatements methods are appropriate.

4.1.6 Comparison of the three processes

The advantages and disadvantages of the three cell types are summarised in Table 4.2.

Table 4.2 Comparison of Electrolytic Cells

	Advantages	**Disadvantages**
Mercury Cells	Proven and well-known technology. Insensitive to production upset conditions. Capacity increase at most existing plants by CD increase. No NaOH concentration required.	Brine purification to remove heavy metals. Products and wastes contain Mercury. Higher energy use. Higher cell maintenance. More shift operators.
Diaphragm Cells	No mercury in products or wastes.	Poor performance during turn-down operation. Mixed product of weak NaOH and brine, which requires extensive treatment. Asbestos waste.
Membrane Cells	Produce high purity NaOH Reduced energy use. No additional toxic materials in products or wastes. More modern technology. Less maintenance. Easier operations. Reduced cell room spacing	Requires very pure brine feedstock. More sensitive to production upset conditions. NaOH needs concentration. Need for higher level of plant personnel. Chlorine product may be contaminated with 2-3% O_2. Special materials of construction

In general, the membrane process should be regarded as the best practicable environmental option for chlorine production. The economics of chlor-alkali plant tend also to favour the membrane process. There is therefore unlikely to be a significant adverse economic impact for new plant based on the membrane process . The mercury and diaphragm cell processes have potentially adverse and long duration environmental concerns, namely mercury and asbestos, that require the implementation of appropriate and extensive BAT to ensure satisfactory environmental performance.

4.1.7 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 silicaceous particles, which must be removed in an extra washing stage, but is otherwise treated as 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. Subsequent handling of chlorine produced by the above process was described earlier in this section. The main difference is that additional front end clean-up of the gases is required.

4.2 Other Halogens

4.2.1 Bromine

Overview

Bromine occurs in abundance in seawater, as sodium bromide, but generally only in very small concentrations. The actual concentration of bromine in seawater varies considerably around the world, being approximately 65 mg/l in the UK. It is also found in the atmosphere, in plant life, in certain rocks and amalgams.

All processes for the manufacture of bromine operate with the same principle: making use of chlorine's higher reduction potential to oxidise bromides to bromine. The steps are:

- Bromides in the brine are oxidised by chlorine to bromine to produce an aqueous mixture of bromine and chlorine in brine.
- Vapour is then stripped from the solution and bromine isolated.
- Purification of the bromine to make other compounds or sell in its liquid state.

Process Description

The normal method of bromine production in the UK uses old technology called the Wilmington process. Free chlorine gas is added to brine to a level of 10% excess over stoichiometry. The brine contains naturally occurring bromides and bromates. Sulphuric acid is added to reduce the pH of the brine to 3-3.5. This stops the formation of further bromates and neutralises the natural hydrogen carbonates. The process is illustrated in figure 4.5. The reaction is summarised below:

$$2NaBr + Cl_2 = Br_2 + 2NaCl$$

The bromine is subsequently separated and purified by absorption in sodium carbonate.

$$3Na_2CO_3 + 2Br_2 + BrCl \rightarrow 4NaBr + 3CO_2 + NaCl + NaBrO_3$$

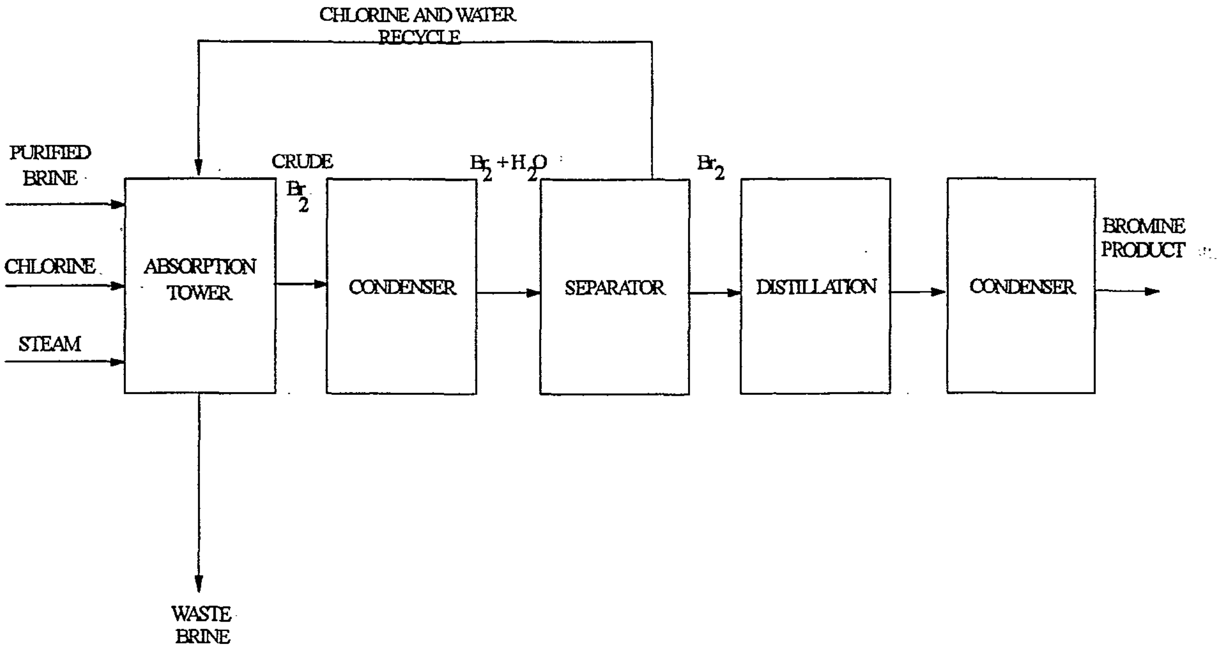

Figure 4.5: Bromine manufacture

Sulphuric acid is then added to the absorbing solution to reconstitute the bromine.

$NaBrO_3 + 5NaBr + 3H_2SO_4 \rightarrow 3Br_2 + 3Na_2SO_4 + 3H_2O$

An improvement to this process is to add sulphur dioxide to the mixture of brine, chlorine and bromine in the blow out tower and to absorb in a water spray. The sulphur dioxide reduces the free halogens to a mixture of hydrobromic, hydrochloric acid. Free chlorine is then reacted with the aqueous solution in a conventional steam out tower and the bromine recovered.

Representative equations are:

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

$$Cl_2 + 2HBr \rightarrow Br_2 + 2HCl$$

Following this stage of chlorine oxidation, the bromine is recovered by vaporisation with steam and condensation to produce an aqueous phase, saturated with bromine, and a separate bromine phase. The crude bromine is separated from the aqueous phase and distilled.

The use of sulphur dioxide results in savings of sodium carbonate and sulphuric acid at the expense of more chlorine and SO_2. The mixture of acids remaining are recycled to be used in the preliminary acidifying of the brine. Sulphur is burned on site to produce the sulphur dioxide, some of which is oxidised catalytically to form sulphur trioxide for making the sulphuric acid.

Bromine may also be produced from waste liquors containing bromine, by stripping, by acidification and finally chlorine oxidation.

Newer Bromine Processing

Patents exist for single and double stage vacuum steam stripping processes for recovering bromine from brines.

The advantage of such processes is reported to be lower steam volumes, less heating, reduced lime treatment of spent brine, lower plant maintenance costs and decreased waste gases. To date the authors are not aware of such processes being in operation. Vacuum processing is unlikely to be introduced in the UK in the foreseeable future.

Releases to Atmosphere

Releases to the atmosphere from this process include those from both the steam out tower and the blow out tower. From the former, sulphur dioxide and free halogens are emitted and from the latter free halogens are released. The same effluents are released to the air from the dibromoethane plant. The releases to atmosphere are scrubbed with caustic soda to keep the levels of chlorine and bromine down. Contaminated acid storage (see below) is also a source of atmospheric releases.

Bromine storage vents are scrubbed by dilute hydrobromic acid which is recycled back to the process. These are backed up with a seawater scrubber to keep bromine releases to a minimum.

Releases to Water

The main unabated release to the water is a large amount of spent brine with a pH of around 3 due to earlier acidification as part of the process. During the process to liberate the bromine from seawater the naturally contained mercury, about 3×10^{-5} mg/l, is separated and subsequently re- released to the sea. Any mercury in the chlorine (from mercury process sourcing) will also be released at the same point. The total extra amount is, however, likely to be low. UK bromine producers currently are not obliged to neutralise the returning depleted brine as there is deemed to be no environmental risk. Some producers worldwide neutralise the brine with ammonia, but the effect of this on the environment is seen to be as damaging as the acidified brine. Another neutralising agent could be considered e.g. caustic, but this is likely to be expensive.

Many streams in this process contain high levels of acid, alkali, or bromine. Most streams are recycled and unrecycled material is collected in the dilute acid liquor tank. The reagents in this tank are then used to supplement the 98% w/w sulphuric acid used to acidify the seawater in the blow out tower.

Releases to Land

The solid wastes derived from the process include chlorides of calcium, sodium, magnesium and potassium which are recovered from the brine during the purification phase. There are also wastes produced by maintenance work. These are disposed of in licensed landfill sites.

4.2.2 Fluorine

Overview

Fluorine is a diatomic molecule existing as a pale yellow gas at room temperatures. It is the most electronegative and hence most oxidising element known. The fluoride ion cannot, therefore, be oxidised to fluorine by the oxidising action of another halogen. It occurs naturally as the mineral fluorspar(CaF_2), which contains about 49% fluorine. Post war, the principal use for fluorine is in the nuclear power industry, where uranium hexafluoride is used to isolate the isotope uranium-235 from its ore. The growth of this industry led to much research and development into ways of producing fluorine on a large scale and today there are several methods, all of which use the same basic principle of electrolysis.

Fluorine and fluorine derived chemicals have a wide and growing range of other uses, including:-

- Fluorocarbons and fluoropolymers.
- High voltage insulation (SF_6).
- Metal coatings industry, where the fluorine is used to gasify difficult materials such as tungsten or ruthenium, for subsequent deposition coating.
- HF for the alkylation of hydrocarbons for blending into gasoline

Fluorine chemicals tend to be high value, low volume products.

Process Description

The main raw material for the production of fluorine on a commercial scale is fluorspar (CaF) as noted above. Anhydrous hydrogen fluoride is produced by reaction of the fluorspar with concentrated sulphuric acid. This process is covered in more detail in Section 4.4.3. The hydrogen fluoride is then charged to the electrolysis cells along with potassium bifluoride, KF.HF to enhance the electrical conductivity to produce fluorine (see figure 4.6).
The principal reactions are:

$$2HF \rightarrow F_2 + H_2$$

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

Fluorine electrolytic cells are classified into three distinct types reflecting differing operating temperature ranges:

- low temperature (-80 to 20°C)
- medium temperature (60-110°C)
- high temperature (220 - 300°C)

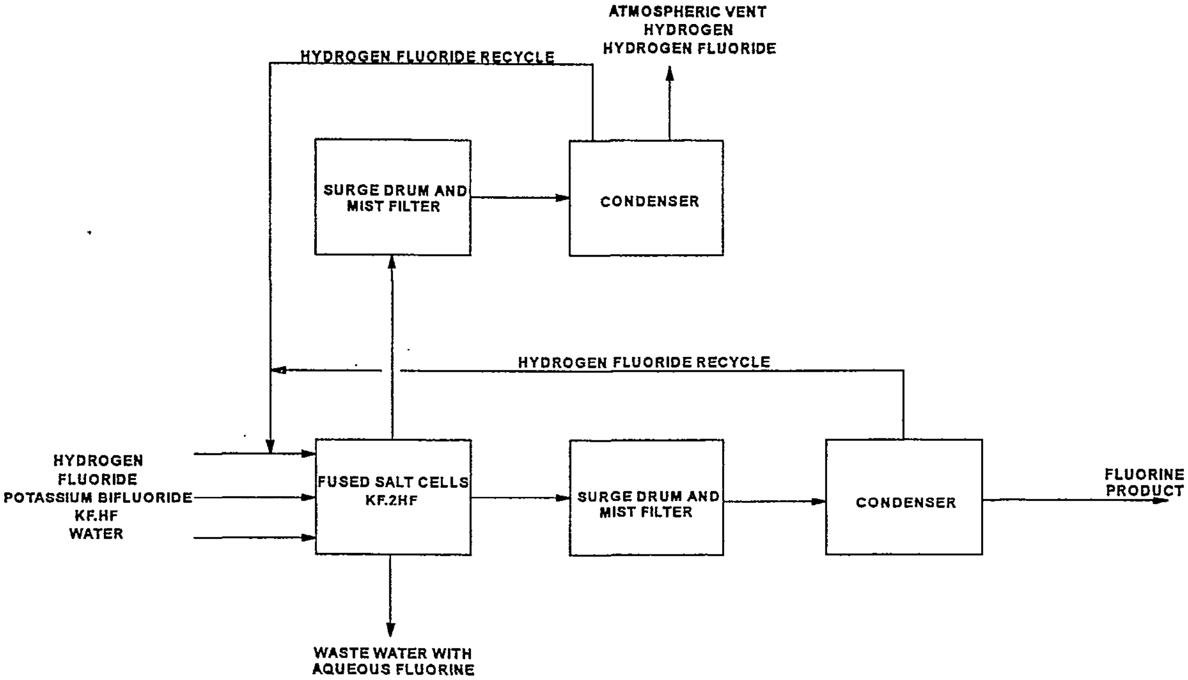

Figure 4.6 : Fluorine production by fused salt electrolysis

The medium temperature process has become the main commercial route as it offers advantages in:

- the vapour pressure of HF above the electrolyte is less
- the process accommodates wider variations in composition of electrolyte
- less corrosion/deterioration of the anode occurs
- tempered water is used as the coolant
- there is reduced formation of resistance filming of the anode (compared with the high temperature process).

The fluoride ion is oxidised at the anode to liberate fluorine gas and the hydrogen ion is reduced at the cathode to produce hydrogen.

A high amperage dc rectifier is used to deliver a steady voltage of ca 12V across the cells connected in series. Hydrogen fluoride is consumed in the electrolysis so must be continually topped up during the process. The cells are cooled with water to maintain temperature in the range 95-105°C.

The gases from each cell are collected in a common header and pass through filters to remove any entrained electrolyte. The hydrogen and fluorine leaving the cell have a hydrogen fluoride content of approximately 10%. Removal of the HF content of the gas streams is achieved by cooling to −110°C. The HF is condensed and recycled to the cells. Further cooling or use of sodium fluoride towers is needed to reduce the HF content to 0.2 mol %, where higher purity fluorine is required.

Environmental Releases

Releases to Air

Emissions to the air from this process are reduced by using suitable scrubbing systems. These are very effective due to the high solubility of fluorine and HF in caustic and water respectively.

The fluorine gas is collected in a common header after generation which is designed to operate at a certain pressure. Any excess production causes overpressure, and some of the gas is relieved to the fluorine scrubber.

There is also a hydrogen fluoride scrubber which is designed to purify any contaminated downstream fluorocarbon product. The scrubbing systems are packed tower type and relieve to the atmosphere. A recirculating solution of potassium hydroxide is used as the absorbent. The spent potassium hydroxide solution is sent to an evaporation pond where any solids are recovered and disposed of to licensed sites. Scrubbing system failure and saturation of the absorbent are potential causes of excursions in emission rates.

The hydrogen generated in the cell is vented to the atmosphere after passing through a potassium hydroxide solution to remove any entrained hydrogen fluoride.

Emission limits are expressed in total amount of free fluorine and hydrogen fluoride in mg/m^3. There are also emission limits on any hydrocarbons released from the site, such as toluene, which are used during the manufacture of fluorocarbons.

Releases to Water

Releases to water occur mainly in the form of releases to the sewer. The aqueous emissions include hydrofluoric acid, potassium hydroxide from the scrubbers, and contaminated surface water collected in the drains. All potential pollutants are sent to sumps on site from where they are pumped to a common sewer.

Some aqueous fluorine compounds will be discharged into the sewer and rivers. The only known method of fluoride removal from aqueous waste is by the use of special precipitation tanks, where the waste is mixed with calcium oxide. The calcium fluoride precipitate should be land filled.

Releases to Land

Solid wastes including product and ventilation filters, unwanted by-products, fluorine cell anodes, calcium fluoride from the treatment of fluoride containing waste waters and evaporation pond solids are disposed of via licensed waste disposal operators.

4.2.3 Iodine

Overview

Iodine is found naturally in brine and some sea-life, such as urchins and seaweed, which extract the iodine from the seawater and store it in higher concentrations. Iodine can, therefore, be recovered from kelp. It is solid at room temperature, and the least electronegative of the halogen group. As a consequence, it is difficult to oxidise but will do so in acid solution. Solid iodine sublimes readily at room temperature. Many chemical compounds can be formed from iodine due to its different stable oxidation states.

Most world production of iodine is by recovery from seawater, where it occurs as potassium or sodium iodides. The amount of iodine in the brine correlates with the salinity of the water. For example, Red Sea brine contains approximately 0.06 ppm and brine from the the Baltic (low salinity) is typically 0.01 ppm. There are other sources at higher concentration; found in conjunction with oil deposits. Iodine is not produced in the UK.

Process Description

The process for the separation of iodine from brine is very similar to that for the recovery of bromine. Iodine rich brine is pumped into a column where it is acidified with hydrochloric acid and then oxidised with chlorine to produce iodine from iodide. Steam strips the iodine from the brine and it is sent to a second column where it is reduced and absorbed in an aqueous solution of hydriodic and sulphuric acids. This iodide solution is removed to a storage tank where chlorine gas precipitates crystals of elemental iodine. The crystals are filtered and dried using sulphuric acid. The acid mixture is recycled.

Environmental Releases and Current Abatement Technology

Iodine has a significant vapour pressure (90.5mm Hg) at its melting point of 113.6°C and may give rise to atmospheric release of iodine vapour through usage and resublimation of iodine and iodine dust.

Abatement of the iodine routinely involves chilling to minimise its vapour pressure, followed by scrubbing with a suitable alkali (sodium or potassium hydroxide). The selection of scrubbing agent will depend on which co-products are likely to be produced.

4.3 Hydrochloric Acid Production

4.3.1 Overview

Hydrochloric acid is normally co-produced with chlorine, hydrogen, sodium hydroxide and sodium hypochlorite, in the chlor-alkali industry. Direct production by burning hydrogen and chlorine accounts for a relatively small portion of production. Most hydrochloric acid is obtained, however, as a by-product of organic chlorination and subsequent cracking processes.

4.3.2 By-Product HCl

The most important source of HCl is the cracking of ethylene di-chloride (EDC) to make vinyl chloride monomer (VCM). By-product HCl generally requires purification to remove the principal contaminants, which depend on the source. Examples include:

- mercury
- chlorinated hydrocarbons
- chlorine
- organic compounds.

Activated carbon may be used to remove chlorine and chlorocarbons, such as chloracetylene. Solid absorbents, such as synthetic zeolites are used to remove toluene and other cyclic compounds. Water may be removed by drying with sulphuric acid.

4.3.3 Direct Production of HCl

Process Description

A direct production plant will comprise three main units: the combustion chamber, the absorber and the scrubber. Chlorine gas is burned in the combustion chamber in the presence of excess hydrogen which forms hydrogen chloride gas. A co-current flow of weak acid passing up the chamber absorbs the gas. Any HCl gas remaining at the top of the absorber is absorbed in the scrubber which is continually fed with fresh demineralised water. The weak acid produced is then used in the main absorber. The strength of the final product is determined by the rate of flow of hydrogen and chlorine to the burner and the flow of water to the scrubber. A typical concentration would be 36.5% w/w hydrochloric acid.

There is considerable amount of heat/evolution and proper provision must be made to ensure a suitable cooling medium is employed.

4.3.4 Environmental Releases

There are very few releases to the air from this process under normal operating conditions. Those that do occur are of hydrogen, chlorine, and hydrogen chloride. Mercury occurs only in trace amounts in the chlorine and hydrogen feedstocks. Two stage caustic and water scrubbing processes may be used to remove any chlorine and HCl from any unburnt hydrogen before releasing it to atmosphere. Recent developments in HCl production include the use of counter current tray scrubbers, which have improved the efficiency of the process.

Some air releases of hydrogen chloride fumes may be generated from the tankers during the filling operations. Tankers should be fitted with their own scrubbing systems to reduce these fugitive releases. Storage tanks should be fitted with caustic scrubbers since strong hydrochloric acid exerts a high vapour pressure.

Aqueous releases are often discharged to a common effluent treatment plant which handles all the aqueous waste from the chlor-alkali processes. The aqueous wastes are often acidic and therefore must be neutralised to some degree before release.

Any small amounts of solid waste may be disposed of to licensed landfill.

4.4 Hydrogen Halides, Oxyhalogens

4.4.1 Hydrogen Chloride

Overview

Anhydrous liquid hydrogen chloride is often used directly for the manufacture of hydrochloric acid. It is also used as a reactant for chlorination in oxychlorination reactions to produce ethylene dichloride.

Process Description

There are several methods of hydrogen chloride manufacture. It may be produced, as a by-product of vinyl chloride monomer manufacture, by passing ethylene dichloride through heated tubes where it is broken down into vinyl chloride monomer and hydrogen chloride. The HCl is then distilled off in liquid form.

It may also be manufactured using the method described above in Section 4.3 whereby hydrogen and chlorine gas are burnt together to produce hydrogen chloride. The emissions to air and water from this process are given above and the abatement technology employed is almost identical.

Another large scale production process for anhydrous hydrogen chloride is by the evaporation of 36% w/w hydrochloric acid. The hydrochloric acid is pre-heated and fed to an evaporator which is a distillation column operating on the falling film principle. The column is heated with steam. Wet hydrogen chloride gas is formed and as it does so the concentration of the hydrochloric acid feed falls until it reaches 20% w/w at the foot of the column. No further evaporation is now possible due to the formation of an azeotrope at these concentrations.

The wet hydrogen chloride then passes to a condenser, where any acid is removed and returned to the column. It then has to be dried and this is achieved by contact with concentrated (98%) sulphuric acid in a glass dryer.

The anhydrous gas is then compressed and liquefied using ethylene glycol as the refrigerant and passed to the drum filling area without intermediate storage.

Environmental Releases and Current Abatement Technology

There are very few emissions from this process. The depleted acid from the bottom of the column is treated with some of the 35% w/w concentrated acid to produce a 28% w/w solution. This is fed into the circulation tank and is used as an absorbent for any releases of hydrogen chloride gas.
The circulation tank has a demineralised packed tower water scrubber attached to it to cope with any emergency relief of hydrogen chloride gas. Any sites of possible escape of HCl gas are also passed through a similar demineralised water scrubber. By this technique, an emission level for hydrogen chloride gas of 10 mg/m^3 is achieved. This is considered to be a suitable limit for a single stage water scrubbing system.

Any fugitive aqueous effluent releases, would be discharged into water courses after treatment in effluent treatment plant. On a hydrogen chloride production plant the ETP would normally serve several different processes. Aqueous effluent from HCl plant principally requires pH adjustment and settling to remove solid contaminants.

Any solid waste would be disposed of to licensed landfill.

4.4.2 Hydrogen Bromide and Hydrobromic Acid

Overview

Hydrogen bromide is a colourless gas that fumes strongly in moist air. The gas is highly soluble in water, forming azeotropic mixtures. At very low temperatures, HBr forms crystalline hydrates. Hydrogen bromide is an important intermediate in forming various organic and inorganic bromides. Hydrogen bromide is prepared commercially in a process similar to the manufacture of hydrogen chloride by the direct gas-phase reaction of hydrogen and bromine.

The basic reaction is:-

$$H_2 + Br_2 \rightarrow 2HBr + \text{heat}$$

Hydrobromic acid is one of the most powerful of the mineral acids. It is a more effective solvent for some ore minerals than hydrochloric acid due to its greaterr reducing action. Hydrobromic acid reacts with metals to form hydrogen. Most metallic construction materials are corroded by HBr and use of special materials is required, e.g. glass lined steel.

Process Description

Hydrogen bromide is formed by burning a mixture of hydrogen and bromine vapour. Platinized asbestos or silica gel may be used to catalyse this reaction. Hydrogen is supplied from cylinders and the gaseous mix carefully controlled to give a stoichiometric excess of hydrogen of 5%. This achieves almost complete conversion of the bromine in the burners. After production the HBr gas is passed through hot activated charcoal or iron to remove the residual free bromine, which is converted to HBr, and is sent for liquefaction and drum filling. Some of the HBr is absorbed in pure demineralised water in a falling film absorber to make hydrobromic acid.

Gaseous HBr is also used to make dibromomethane (DBM) and bromochloromethane (BCM) by reaction with dichloromethane in the presence of a catalyst. Hydrogen chloride is produced as a by-product . Any unreacted dichloromethane is returned to the reactor via feed tanks.

Environmental Releases and Current Abatement Technology

Environmental emissions to the atmosphere from this process include bromine and hydrogen bromide.

Non-absorbed gases from the absorber are scrubbed before release. Hydrogen bromide releases are reduced by scrubbing vent gases with sea water before venting to the atmosphere. Hydrobromic acid/ water or caustic systems are also effective in scrubbing gaseous HBr.

Hydrobromic acid storage vessels breather valves should be fitted with caustic scrubbers to prevent fugitive hydrogen bromide emissions. A central collection system may be used to link any point of release from the plant to a caustic scrubbing unit.

The wet hydrogen bromide gas produced is dried using molecular sieves which must themselves be routinely dried using heated air which is subsequently discharged to atmosphere via seawater scrubbers. Nitrogen is used to purge the dryers before reinstatement and is also used as a sealant for various pieces of equipment on site. There may, therefore, be nitrogen releases to atmosphere contaminated with HBr. Hence scrubbing will be needed. Achievable levels for bromine and hydrogen bromide using such scrubbing systems are 10 mg/m^3 and 5 $mg/^3$ respectively.

Small amounts of dibromomethane, bromochloromethane and dichloromethane may also be released during their manufacture and will require scrubbing before discharge.

Aqueous emissions are generally routed to the sea from such a bromine plant and are carefully monitored. They include bromine, hydrogen bromide, hydrogen chloride, and some halogenated hydrocarbons such as those listed above. These come mainly from the caustic scrubber liquor treatment area where the contained bromine compounds are effectively converted back to bromine.

The design, operation and instrumentation of the scrubbing systems should be very effective at reducing HBr emissions in view of the negligible vapour pressure of hydrogen bromide above alkaline solutions of the correct strength. Thus the concentration levels for releases into air of HBr as suggested at the beginning of this section should be maintained.

Emissions to land occur generally from maintenance and packaging activities. Solid wastes require disposal to licensed land fill or by incineration.

4.4.3 Hydrogen Fluoride and Hydrofluoric Acid

Overview

Anhydrous hydrogen fluoride exists as a colourless liquid with a low boiling point; fuming readily in air. It is highly soluble in water where it forms strong and very corrosive hydrofluoric acid solution. Aqueous HF is powerful enough to dissolve silicon and is used in glass etching. Both hydrogen fluoride solution and vapour may cause very serious burns to organic tissue due to their rapid reaction with bone calcium. Such burns will require immediate specialist medical attention. The production of hydrogen fluoride involves, in principal, the reaction of fluorspar (calcium fluoride) with sulphuric acid. If anhydrous HF is required, the associated water of crystallisation, must be removed.

The manufacture of hydrogen fluoride and hydrofluoric acid involves essentially the same reaction, between fluorspar and sulphuric acid.

Process Description

The reaction between fluorspar and sulphuric acid is illustrated below:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

Wet fluorspar CaF_2 is loaded onto a belt conveyor and fed into a dryer combustion chamber, where the fluorspar is dried in a hot gas stream. The resulting powder is transferred to a silo for stoarage and the gas filtered before being released to the atmosphere via a stack.

A preheated mixture of fluorspar, recycled sulphuric acid, oleum and fresh sulphuric acid is fed into the pre- reactor where it is mixed with finely ground calcium fluoride to form a thin suspension. This is heated up to initiate reaction between the fluorspar and the acid. The suspension thickens to form a paste, often sticky. Modern furnaces, typically rotary, are designed to cope with this material and produce a flowable dry solid (calcium sulphate) as the reaction proceeds to completion. The rotating kiln is heated to between 300 and 350°C, using an external jacket and operates under a slight vacuum.

As the solids are heated, HF gas is evolved along with gaseous contaminants. The solid calcium sulphate is acidic and requires neutralisation with calcium hydroxide. The solids are then crushed and air conveyed to silos ready for landfill. Alternatively the calcium sulphate may be utilised as a co-product for building materials.

The overall yield of HF is typically greater than 90% and depends largely on the impurities in the fluorspar. A typical acid grade fluorspar would be 97% calcium fluoride with silica and calcium carbonate being the major contaminants (between 0.5 and 1%). Other impurities could include traces of metal oxides (eg ruthenium oxide), sulphur chloride and ppm levels of arsenic. Organic carbon and phosphorous compounds may also be present.

Silica has the greatest impact on yield losses, based on the chemical stoichiometry of the fluorosilicic acid.

$$SiO_2 + 3H_2SO_4 + CaF_2 \rightarrow H_2SiF_6 + 2H_2O + 3CaSO_4$$

For each 1% silica, the fluoride and sulphuric acid losses are 3.9% and 4.9%, respectively.

It should be noted that the proportion of sulphuric acid to oleum used in the reaction is determined by the water balance. The water reacts with the SO_3 component of the oleum to produce additional sulphuric acid.

$$H_2O + SO_3 \rightarrow H_2SO_4$$

The HF gas is extracted and any entrained solid particles are removed. The gas is then dried and cooled by contact with sulphuric acid in the pre-scrubbers. This cooled gas is sent for further cooling and condensation and the produced liquid product is separated from any light ends by distillation. The anhydrous HF is then sent to storage.

Treatment of the HF gas to produce hydrofluoric acid is essentially the same, except a rectification stage is involved. The HF gas produced is removed, filtered and freed from high boiling point impurities. It is then liquefied by removing heat through indirect contact with chilled water and stored in a crude acid tank.

The concentrated acid, (99.9%) is produced when the crude acid is treated in a rectifying column designed to remove the low boiling substances, sulphur dioxide and fluorosilicic acid, which are removed overhead and the concentrated acid is transferred, via further cooling, to storage. This concentrated acid may then be diluted for sale to between 60-75%,

Environmental Releases and Current Abatement Technology

There are potentially several releases to the atmosphere from this process. The gases from the condensation and rectification stages are fed to a sulphuric acid scrubber where some of the contained hydrogen fluoride is recovered. The remaining light ends with HF gas are passed through water spray columns and a final central absorption water scrubber prior to discharge to the air at a suitable elevation. Hydrogen fluoride gas is very soluble in water which is the ideal scrubbing medium as the dilute HF from the scrubber should be suitable for recycle.

The fluorspar and calcium hydroxide silos produce dust during filling and, therefore, the displaced air from these silos should be passed through dust filters.

Conveyor air, used to transport the crushed solid waste to the silos for subsequent landfill, has to be passed through a water scrubber to remove any entrained solids before it is released into the atmosphere.

There are low levels of emissions of other chemicals used or produced at various stages of the process. These include sulphur dioxide gas and sulphuric acid vapour. Hydrogen chloride gas is also emitted in small quantities.

The gas burners for the rotary kiln may produce CO during incomplete combustion and will produce some nitrogen oxides.

Most of the kilns have an emergency gas evacuation scrubber fitted which is independent of any others. This may be operated manually or automatically on kiln overpressure. The gas scrubber is used to clean the vent gases before discharge.

The aqueous effluents are dealt with in a central effluent treatment plant. This unit takes waste from all areas for neutralisation before discharge under consents. Acidic solutions are received and neutralised using a slurry mixture of calcium oxide, sodium hydroxide and water. Vapours produced in this aqueous neutralisation stage are discharged to atmosphere at a suitable height via a caustic scrubber.

It is important that the supply of fluorspar is as pure as possible as some sources may contain a high percentage of silica. During the reaction this silica evolves fluorosilicic acid (H_2SiF_6) which is the main route of fluorine loss for the process. Therefore, to minimise this problem and to reduce the load on the scrubbers, the silica content should be minimised. Fluorosilicic acid is easily recovered and may be used as a by-product for water fluoridation. Alternatively it will require disposal, after neutralisation.

There will also be aqueous releases of scrubber liquors, both water and alkali, and any spills on site will be lost to drain.

Solid waste calcium sulphate (anhydrite) can be sold or deposited in landfill where it may be used as an encapsulation agent.

4.4.4 Potassium Iodide

Overview

Potassium iodide is used as an additive in cattle feeds; as a chemical used in the photographic industry; in sanitation and also administered for treatment of radiation poisoning following a nuclear accident. The most common method of manufacture is by reaction of flaked iodine and potassium hydroxide. This product is then recovered by crystallisation from water.

Potassium Iodide Process Description

The stoichiometric reaction involved in the production is illustrated below:

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

Approximately 80% of the iodate crystallises and is processed as a by-product. Of the remainder, 90% is decomposed to iodide through evaporation and heating of the iodate solution in a gas fired furnace.

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

This fused potassium iodide is dissolved in water and purified by pH adjustment with CO_2. Barium and potassium carbonate, hydrogen sulphide and iron iodide are then added to precipitate sulphates and heavy metal impurities. The potassium iodide is recrystallised from solution using specially designed apparatus and then dried and packaged.

Environmental Releases and Current Abatement Technology

Due to its high vapour pressure at its melting point, iodine readily sublimes. As a result of this, the principal gaseous release occurs during the charging operation. This may be reduced significantly by chilling the vapours with refrigerated brine and recycling the recovered iodine. Residual vapours may be removed by passing the vapours through potassium hydroxide scrubbers and recycling the scrubber liquor back to the process. The scrubbed gases then pass to air via a suitably sized stack and typically contain $<0.1\ \mu g/m^3$.

Where fuel firing is used during the iodide recovery, NOx and SOx will also be released to the atmosphere, and may require abatement.

Waste water from a potassium iodide plant is likely to to be contaminated with traces of raw materials and products, including the precipitated heavy metals and sulphates and the precipitating chemicals. Provided the iodine compounds are recovered, the actual amount released to the environment is small. Another source of waste water will be from the production area wash down and the clean-up of spills. These can be expected to contain a range of the above mentioned chemicals and should be directed through the effluent treatment section.

Solid releases from this process include solid waste slurries and purification sludges which arise during the precipitation of impurities. These wastes are either dealt with by a licensed contractor or sent to authorised landfills.

4.4.5 Sodium Hypochlorite

Overview

Sodium hypochlorite solutions are used primarily in the paper and textile industries for bleaching. The use of chlorine dioxide is generally displacing sodium hypochlorite in these industries. On the other hand, the use of electrochemically produced dilute hypochlorite solutions has increased largely recently. Electrolytic generators can be used in situ, where hypochlorite is needed for disinfection or for bleaching, especially for locations remote from chlor-alkali plants. Additionally, transport over long distances should be avoided to minimise decomposition of the hypochlorite increasing the attractions of on-site dedicated hypochlorite generators. Applications include:

- biofouling
- control of sea water
- supply of 'chlorine demand' for various facilities such as swimming pools and ocean aquariums.

Brief process descriptions of sodium hypochlorite production processes are provided below along with methods of abatement for any releases to atmosphere.

Process Description

A sodium hypochlorite unit is generally attached to each chlor-alkali plant to remove residual chlorine from tail gas achieved by circulating caustic soda through a packed column through which the tail gas is passed. The sodium hypochlorite solution is regarded as a co-product of the chlor-alkali process.

An alternative method of producing hypochlorite solutions is by on-site dedicated electro-synthesis, and this is practised at a number of sites in the UK. The sodium hypochlorite is manufactured by the reaction of chlorine, released by the electrolysis of a saturated brine solution, with a bleed of the co-product sodium hydroxide solution.

A typical process takes place in three stages. Brine is prepared by dissolving high purity salt in treated water, followed by removal of the remaining undesirable metal ions by ion exchange beds. Electrolysis is then carried out in special cells which utilise a proprietary membrane. Hydrogen produced by electrolysis is vented to atmosphere via a stack. The chlorine produced by electrolysis is immediately reacted with a bleed sodium hydroxide solution (produced by the cells) to yield the product sodium hypochlorite solution. The process is essentially similar to the chlor-alkali process except that the chlorine and sodium hydroxide products from electrolysis are immediately utilised to make sodium hypochlorite. A further method of production is by the vaporisation of liquid chlorine into a purpose-built scrubber. The reaction is very exothermic and heat extraction from the circulating caustic may be required. Sodium chlorate production has to be minimised.

Long term storage of hypochlorite solution may be problematic as the solution is likely to decompose, particularly in the presence of certain metals. The solution should be maintained above pH 11, to minimise decomposition. Contact with heavy metals (Ni, Co, Cu, Fe) catalyses decomposition. Hence materials used for plant and equipment are commonly high performance plastics or rubber-lined steel.

Environmental Releases and Current Abatement Technology.

Chlorine releases to atmosphere are scrubbed using caustic scrubbers.

Two gas scrubbing systems are typically installed for an on-site electrochemical dedicated process.

Chlorine residues are removed from the acidified spent brine by bubbling air through it, and absorbing the chlorine in a process gas scrubber. The exhaust gases from this process gas scrubber can be vented to atmosphere via a second emergency scrubber. Plant room ventilation vapours can also be directed to this second scrubber if any trace of chlorine gas is detected inside the plant room. There are thus three vents to atmosphere for this typical process:

- Hydrogen vent from electrolysis cells
- Potential chlorine containing vent from the process gas scrubber
- Potential chlorine containing vent from the emergency scrubber

All liquid wastes, except acidic wastes, are directed to the first collecting tank and where necessary are treated with sodium thiosulphate to minimise free chlorine. Acidic liquid wastes are directed to a separate second collecting tank and are neutralised prior to transfer to the first collecting tank. The treated liquid wastes from the first collecting tank are then discharged as aqueous waste.

4.4.6 Chlorine Dioxide

Overview

Chlorine dioxide is a greenish-yellow gas with a pungent odour. It can be condensed to a reddish-brown liquid at 11 °C and is an extremely unstable gas, readily decomposing to chlorine and oxygen even on mild heating. It is explosive as a gas or liquid at high concentrations. However, it can be handled easily when diluted with air to less than 15 vol% and it is easily soluble in water.

Chlorine dioxide is a widely used oxidising bleaching agent, in particular for high quality cellulose. A trend has been to reduce the use of chlorine and aqueous hypochlorite as bleaching agents and to replace them with chlorine dioxide. It is used in the pulp and paper, textile and food industries. It also finds use as a disinfectant in the sanitisation of industrial and municipal waters and sewage.

The explosive nature of the gas prevents its transportation. Thus, it is manufactured near to its point of use and usually absorbed in water (at about 6-10 g/l) for storage and process use.

The various methods of chlorine dioxide manufacture are described below. As well as being unstable and explosive, chlorine dioxide is most toxic to personnel at concentrations higher than 1ppm. Thus plant design, operation and monitoring requirements must be such as to provide a safe working environment both within and outside the plant boundary. Where there are potential releases of chlorine and HCl, then these are controlled by the necessary abatement systems as reviewed in Sections 4.1, 4.3 and 4.4.

Process Description

Sodium chlorite is the preferred raw material for chlorine dioxide production where quantities are less than about 2 tonnes per day. This is typical for water treatment and disinfection applications. Chlorine gas can be passed through a sodium chlorite solution:

$$2NaC1O_2 + Cl_2 = 2\ NaCl + 2\ C1O_2$$

The alternative reaction of sodium chlorite solution with hydrochloric acid is also commonly used.

$$5\ NaClO_2 + 4\ HCL = 4\ ClO_2 + 2\ H_2O + 5\ NaCl$$

Other applications not requiring high purity (ie. chlorine free) chlorine dioxide use chemical generation methods, e.g. reacting sodium chlorate and hydrochloric acid, sulphuric acid and mixtures containing sodium chloride. High conversions of chlorate can be achieved by the addition of large excesses of acid and a reducing agent.

Large amounts of chlorine dioxide are used in pulp bleaching and smaller quantities are used for the manufacture of sodium chlorite. In these applications, sodium chlorate is the predominant commercially available raw material. Chlorine dioxide production from sodium chlorate is achieved by the reduction of the chlorate ion in the presence of strong acid. The reaction consumes acid, so that acid and reducing agents must be constantly added to maintain the reaction.

In industrial chlorine dioxide production, the main reducing agents used are sulphur dioxide, hydrochloric acid or methanol.

Licensors have developed integrated systems that combine chlorine dioxide production (using hydrochloric acid as reducing agent) with the production of chlorine, caustic soda and hydrochloric acid. Such combined systems can use sodium chloride and electric power as raw materials producing chlorine dioxide solution and caustic soda.

Another licensed process, used extensively, converts sodium chlorate, sodium chloride and sulphuric acid to chlorine dioxide.

Other processes use sulphur dioxide or methanol as the reducing agent. Electrochemical reduction methods, for producing pure chlorine dioxide from acidic solutions containing sodium chlorate, have also been developed.

High chlorine dioxide usage in pulp mills, and the need for chlorine-free chlorine dioxide, are driving forces for future process and design changes in commercial generator systems using sodium chlorate. Alternative developments are now considering the use of chloric acid as generator feed in place of sodium chlorate, thus reducing the requirement for acid addition.

Environmental Releases and Current Abatement Technology

Chlorine dioxide gas is toxic and hazardous. Human and animal organisms are extremely sensitive to chlorine dioxide when exposed to concentrations higher than 1ppm. However, chlorine dioxide levels below 0.1ppm are relatively harmless.

Chlorine dioxide production plants should be operated at slightly sub-atmospheric pressure. The plant design must also account for the explosive nature of chlorine dioxide and chlorine dioxide should be diluted in the air to below 15% before leaving the generator. It is not advisable to transport chlorine dioxide over long distances in any form.

Chlorine dioxide solutions are normally stored cold at concentrations of less than 10 g/l in order to keep the concentration of gaseous chlorine dioxide above the aqueous solutions below the explosive limit.

Potential releases of chlorine, hydrogen chloride gas or hydrochloric acid should be controlled by the necessary abatement systems as reviewed in Sections 4.1, 4.3 and 4.4.

4.4.7 Phosgene (Carbonyl Chloride)

Overview

Phosgene (or carbonyl chloride) is a colourless gas, which condenses at normal pressure at about 8°C to form a colourless liquid.

The importance of phosgene (apart from its historical use as a poison gas in World War 1) is in the production of synthetic intermediates in different fields of chemistry, and particularly in the manufacture of di-isocyanates used in the preparation of polyurethanes.

Because of its high toxicity and wide range of commercial applications, great efforts have been made worldwide to ensure safe handling of phosgene. Thus, for instance, the storage and transportation of phosgene are avoided as far as possible for safety reasons, and most phosgene manufacture is captive i.e. it is used in the manufacture of other chemicals within the same site boundary.

Process Description

Phosgene is obtained commercially by passing carbon monoxide and chlorine gas over a catalyst such as activated carbon. A high level of automation is provided for phosgene purification, condensation and storage. Because of its toxicity, extensive safety procedures and safety equipment are incorporated in plant design and operation.

The main manufacturing steps are preparation and purification of the feedstocks (carbon monoxide and chlorine); reaction of the mixed feed gases over the catalyst; purification and condensation of phosgene and the recovery of traces of phosgene from residual gases to ensure operator and environmental safety.

The carbon monoxide and chlorine feeds must be as dry and as pure as possible to avoid corrosion of equipment and the generation of undesirable by-products. The reaction is rapid and strongly exothermic so that efficient heat removal is required. The product gases are cooled to liquefy phosgene and uncondensed gases are then scrubbed to remove the residual phosgene. In some cases the uncondensed phosgene is absorbed into a solvent in an absorption column. The solvent used for the absorption is typically the same solvent as is used in the downstream process step. The remaining non-absorbable gas stream is fed to a waste gas treatment system to be freed of residual phosgene

Environmental Releases and Current Abatement Technology.

The residual gases must be freed from phosgene in a decomposition unit. Various methods are used in practice:

a) Decomposition by Caustic Scrubbing

The residual gas is led through packed towers where sodium hydroxide solution is introduced at the top of the towers. Venturi scrubbers may also be used. Make-up sodium hydroxide solution is added under pH control. A series of scrubbers may be used to provide additional security against phosgene releases.

b) Decomposition in Activated Carbon Towers

The residual gas is passed through towers packed with activated carbon with water being fed to the top of the towers. The concentration of hydrochloric acid (formed by decomposition of phosgene) is kept below 10% to maintain the reaction efficiency . This is achieved by balancing the make-up water and hydrochloric acid before the stream is taken-off. For safety reasons, two towers are frequently used in series.

c) Combustion

The residual gases are burnt to convert any phosgene to carbon dioxide and HCl. An advantage of this method is that all remaining pollutants in the residual gas (such as solvents and carbon monoxide) are burnt together with phosgene, but the combustion flue gas will contain HCl vapour and, possibly furans and dioxins. Correct furnace design and operation is essential to minimise these pollutants. A system for scrubbing should also be provided. Environment Agency Guidance Note IPCGN S2 5.01 “Waste Incineration” provides details of controlling these chemicals.

Normally the outlet gas from the phosgene destruction equipment is continuously monitored for residual phosgene content to ensure complete destruction or decomposition.

Releases to water comprise sodium carbonate, sodium chloride and sodium hydroxide from scrubber liquors.

Spent catalyst from the phosgene reactor constitutes the main release to land.

4.4.8 Aluminium Chloride

Overview

Anhydrous aluminium chloride is a white solid that readily reacts with any moisture in the air. Commercial grades vary in colour from light yellow to light grey as a result of impurities. At atmospheric pressure, anhydrous aluminium chloride sublimes at 180°C to the vapour phases, and the liquid form only exists at elevated temperatures and pressures.

Aluminium chloride is used as a catalyst in a wide variety of organic manufacturing processes, such as Friedel-Crafts and allied reactions in the synthesis of agricultural chemicals, pharmaceuticals, detergents and dyes. Aluminium chloride is also used as a nucleating agent in the chloride process for titanium dioxide.

Process Description

Anhydrous aluminium chloride is generally manufactured by the reaction of chlorine vapour with molten aluminium. The aluminium can be of varying purity. The reactor temperature is controlled between 600-750°C. Chlorine is fed into the molten aluminium pool below the pool's surface. Aluminium chloride sublimes from the pool and into the condensing vessel, where the product solidifies onto the condenser walls. Condensers are normally air-cooled, vertical cylinders with cone-shaped bottoms. The aluminium chloride grows into crystals, which are periodically removed, crushed, screened and packaged under a dry air or nitrogen atmosphere. The product may be coloured yellow due to the presence of excess chlorine or ferric chloride.

Anhydrous aluminium chloride reacts vigorously with water or moisture. Thus, exposure to humid air must be prevented and safe handling procedures must be adhered to.

A number of other processes can also be used for the production of aluminium chloride. Chlorination of alumina (pure aluminium oxide) has advantages over the formerly widely used bauxite process and avoids the high raw material costs involved in metal chlorination. However, most anhydrous aluminium chloride worldwide is now made by chlorinating aluminium metal.

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.

Environmental Releases and Current Abatement Technology.

Anhydrous aluminium chloride reacts with water or moisture, generating heat, steam and hydrochloric acid vapours. Product handling and storage facilities must therefore prevent any contact with moisture.

Fumes resulting from the exposure of anhydrous aluminium chloride to moisture are corrosive and acidic. Collection systems should be provided to conduct aluminium chloride dusts and vapours to a scrubbing system, which can range from single packed tower scrubbers to sophisticated high energy devices such as Venturi designs.

Spills should be picked up before flushing thoroughly with water and neutralising with soda ash or lime. The flushing water should be directed to effluent treatment.

Releases of chlorine to air can be minimised by a) ensuring that reactor conditions are such that virtually all chlorine fed to the reactors is converted to aluminium chloride, and b) by the use of dedicated sodium hydroxide scrubbers e.g. one on the chlorine storage facility and another for chlorine emissions from the rest of the plant. Releases of hydrogen chloride can be minimised by ensuring that aluminium chloride does not contact moist air, and by the use of water and sodium hydroxide scrubbers. Standby scrubbers can be available for use in the event of failure of a main scrubber. The waste liquid effluent containing hypochlorite from the caustic scrubber can be catalytically treated to make a brine solution.

Other releases to water include soluble aluminium compounds removed as hydroxides. Inert impurities from the aluminium feed material which have to be periodically removed from the furnace are the main release to land. The PAC process releases spent hydrated alumina.

4.4.9 Ferric Chloride

Overview

Anhydrous ferric chloride is not manufactured in the UK, but ferric chloride solutions are produced for use as flocculating and precipitating agents in water treatment. Ferric chloride is particularly effective in municipal and industrial waste water treatment. It is used to precipitate out sulphides and contaminants such as oils and polymers. They are absorbed onto the iron hydroxide flocs but are otherwise difficult to degrade . Preliminary treatment with ferric chloride can increase the capacity of overloaded clarifier plants.

Sludge conditioning with ferric chloride and lime improves the dewatering of filter sludges, so that sludges are drier and better suited to incineration or other disposal.

In the UK, ferric chloride solutions are generally manufactured from spent pickle liquors (containing ferrous chloride) and chlorine feedstocks. The process plant can be batch type or continuous type.

Process Description

General

Pickle liquor, consisting of ferrous chloride (20-25% w/w) and hydrochloric acid (2-8% w/w) is a waste product from the steel industry. It may be converted to the ferric form by treatment with steel, either by batch reaction or in a continuous reactor.

Batch Process

Steel feedstock is in the form of waste punchings. Chlorine gas feedstock may be supplied by pipeline. In the process raw feedstock material (spent pickle liquor) is treated with chlorine gas until the end point of conversion to ferric chloride is indicated by the instrumentation system. There is the potential for release of chlorine to atmosphere and chlorine detectors should be used to detect a chlorine release and trigger interlocks and alarms on the chlorine supply system. A vent gas scrubbing system may be necessary to limit releases.

Continuous Process

In the continuous process, the plant will consist of a steel dissolver, a packed ferrous tower with a circulating liquor of ferrous chlorine and a packed ferric tower with a circulating liquor of ferric chloride. Pickle liquor and chlorine are passed counter currently through the process. The pickle liquor is fed in at the ferrous end and the chlorine is fed in at the ferric end. The product, 41% ferric chloride solution, is removed from the ferric tower system. Gases resulting from the process are discharged to atmosphere from the ferrous chloride tower system via a stack as the ferrous tower is a very effective scrubber. The waste stack should be monitored continuously for chlorine and should incorporate a plant trip.

Direct Chlorination

In the literature, references are made to anhydrous ferric chloride production by reaction of dry chlorine with scrap iron in a shaft furnace at 500-700°C. This type of process is known as direct chlorination. In another such process, iron scrap and dry chlorine gas react in eutectic melt of ferric chloride and potassium or sodium chloride. However, there are no direct chlorination processes in the UK.

Environmental Releases and Current Abatement Technology.

There is potential for release of chlorine gas to the atmosphere from the processes which utilise chlorine gas as a feedstock. Chlorine detectors should enable the operator to detect when a release of chlorine occurs, and to take appropriate counter measures. BAT should be considered as directing off gases, containing chlorine, through an appropriate scrubbing system. There are no significant releases to water. Sludges which accumulate in reaction vessels are periodically disposed of off-site, as 'special wastes' to licensed landfill.

4.4.10 Lithium

Overview

The largest application of lithium metal is in the production of organo-lithium compounds, principally butyl lithium and lithium hydride. A rapidly growing application of lithium metal is in sacrificial anodes in batteries. The main advantages of lithium batteries are high power output, extremely good storage properties (low rate of self-discharge) and relatively small power loss at low temperatures.

Process Description

Lithium metal is currently produced by the electrolysis of molten lithium chloride, whose melting point is lowered by the addition of potassium chloride. The eutectic mixture is maintained at about 450°C, using gas fired burners and electrolysed to lithium metal and chlorine gas.

During the manufacture of lithium based organometallic chemicals, lithium chloride and lithium metal can also be manufactured for sale, as well as sodium hypochlorite as a byproduct.

Lithium carbonate feedstock is reacted with hydrochloric acid to form lithium chloride. This is concentrated, crystallised and dried. There are potential releases to air of hydrogen chloride from this process and so vents to air are passed via a dilute caustic soda scrubber.

Chlorine gas is removed from the cells and is scrubbed with sodium hydroxide to produce sodium hypochlorite. Lithium metal is removed from the surface of the cell and cast into ingots which can be coated with mineral oil to prevent contact with air during storage. There are potential releases to air of chlorine gas from the chlorine scrubber.

Environmental Releases and Current Abatement Technology

As indicated above, there are potential releases to air of hydrogen chloride and chlorine gas, so suitable scrubbers are used to reduce emissions to air of these substances. Suitable monitoring instrumentation should be used to ensure that releases to air do not exceed allowable concentrations and/or quantities of these substances.

Alternatively for environmental releases and current abatement technology also applicable to these substances, are covered in section 4.1 for chlorine releases and to sections 4.3 and 4.4 for hydrochloric acid/hydrogen chloride releases. When impurity levels in the eutectic mixture of lithium and potassium chloride reach an unacceptable level, the spent eutectic requires periodic disposal as "special waste" to landfill.

5. TITANIUM DIOXIDE MANUFACTURE

5.1 Overview

Titanium dioxide is a widely used pigment with demand closely linked to growth in housing, the automobile and the coatings industries. There are principally two commercial processes for TiO_2 manufacture, both of which are the subject of an EC Directive (92/112/EEC 15 December 1992):-

- the sulphate process, described in section 5.2
- the chloride process, described in section 5.3

In developing this section, the authors drew significantly on the United Nations paper, "Use and disposal of wastes from phosphoric acid and titanium dioxide production"; updating information in that paper to reflect latest abatement technology trends.

5.1.1 Feedstocks

The sulphate route has some advantages since it can use ilmenite, a lower grade ore, as its titanium source instead of the purer and scarcer rutile. In particular, ores at a concentration of 45-60% TiO_2 or titanium-rich slags (70-85% TiO_2) are readily attacked by sulphuric acid. Weathered ilmenite ores, with higher TiO_2 concentrations (in excess of 60%) have reduced reactivity with sulphuric acid and are less useful. Ilmenites containing high levels of transition metal impurities, or unacceptable levels of thorium and uranium, are also not used in the sulphate process. Additionally the increased presence of impurities leads to more waste from the process. The sulphate process may be operated to produce either of the crystalline forms of the TiO_2, rutile or anatase.

The chloride process is able to 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, as impurities, e.g. iron, in the ore feed result in a loss of chlorine in the form of iron chloride. The chloride process only produces the rutile form of TiO_2.

5.1.2 Production

Table 5.1 shows world-wide production of sulphate and chloride forms of TiO_2 between 1971 and 1996.

Table 5.1 World production of TiO_2, tonne x 10^3

Year	Sulphate Route	Chloride Route
1971	1734	330
1981	1768	885
1996	1789	2267

The figures show that the main growth in TiO_2 production has been from the chloride process. From 1971 to 1996, the world-wide production of TiO_2 by the chloride process increased significantly from 330,000 tpa to 2,267,000 tpa, while there was virtually no change in the world-wide sulphate route production capacity. In practice, the sulphate process has dropped from 85% of total capacity in 1971 to 44% in 1996 and is forecast to account for 35-40% by 2000.

It is clear that most new TiO_2 plant capacity in the future will be based on the chloride process, as it is less capital intensive than the sulphate process, despite its more sophisticated technology. However, this may lead to feedstock supply problems as the preferred rutile ore feedstock is already in limited supply. More attention may in future be directed towards making available increased supplies of synthetic rutile feedstocks. It is concluded that the chloride process will continue to be preferred for new TiO_2 plants to be constructed in the future, although modern sulphate process plants will continue to operate for those applications to meet a niche demand for the 'softer' toned pigment.

5.1.3 Product Characteristics

There are differences in the product performance characteristics of TiO_2 produced by the sulphate process, compared with the chloride process.

The sulphate process TiO_2 tends to have "softer" optical properties and is the product of choice in applications such as fibres, fine papers and printing inks, whereas TiO_2 produced by the chloride process is more suitable for use in pigment production. In particular, pigments used in demanding applications are almost always subjected to after treatment to improve weather resistance, and dispersibility of the pigment. The specific properties of chloride process titanium dioxide pigment, which are of major importance to the user, are dispersibility, texture, optical properties and durability.

In between, the above applications, there is a broad range of uses where high quality TiO_2 produced by either route is equally suitable

5.1.4 Abatement

Both processes generate wastes from the ore residues, but recent developments have included process changes to ensure TiO_2 plants meet pollution abatement requirements. As a result of these developments, both processes are generally able to satisfy and even improve upon strict environmental limits, such as those set by the EC Directive (92/112/EEC 15 December 1992).

For the sulphate process, selection of abatement techniques depends on feedstock selection, methods for handling spent sulphuric acid solutions (e.g. by reconcentration and recycling of the acid), and utilisation of the ferrous sulphate waste. These are described in more detail in Section 5.2.

Abatement techniques for the chloride process include feedstock selection, methods for the recovery and recycle of chlorine and utilisation of the various metallic chloride by-products. These are described in more detail in Section 5.3.

5.2 Sulphate Process

5.2.1 Process description

The process generally consists of the following sequential stages (see figure 5.1 for a typical block flow scheme).

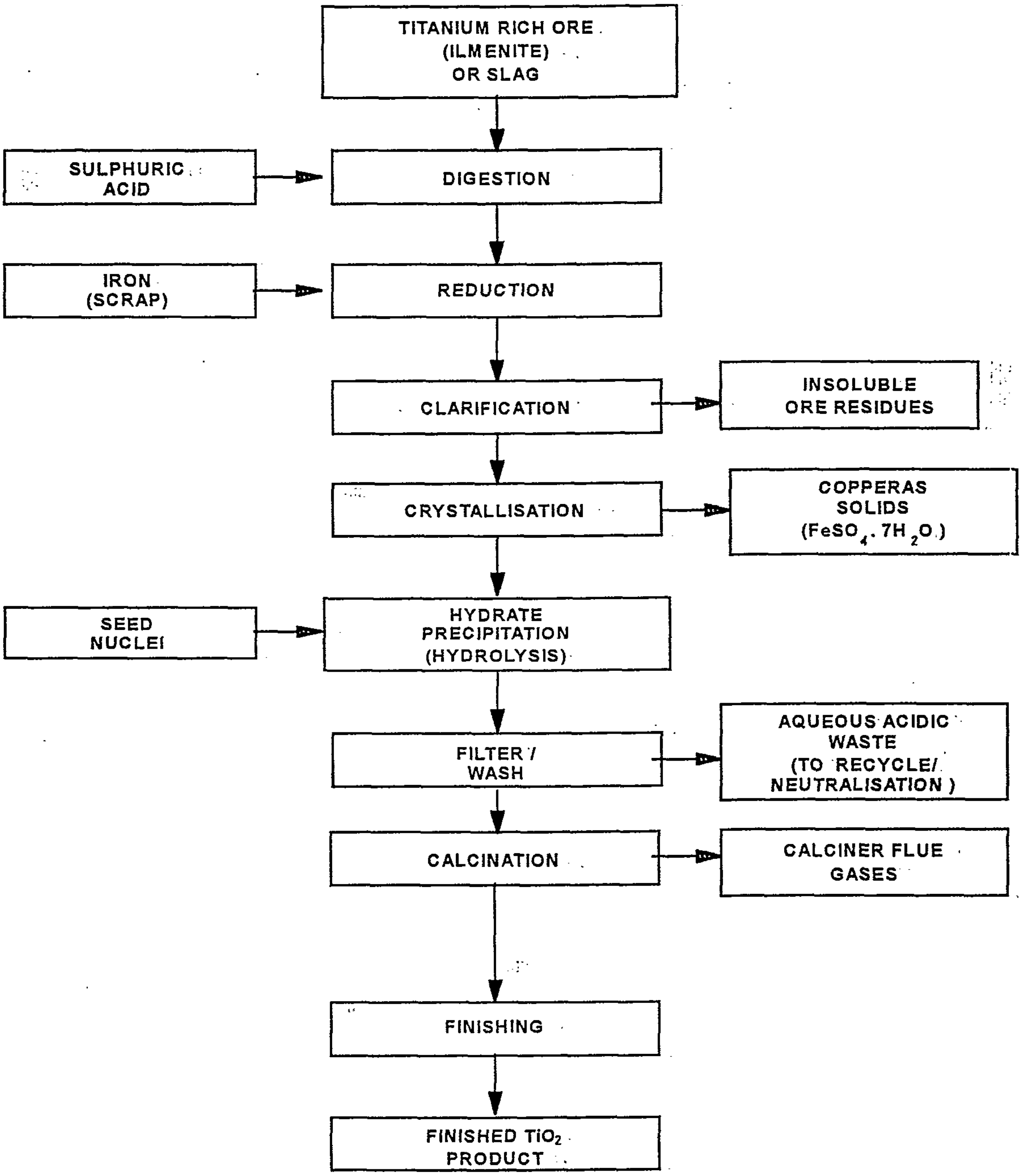

Figure 5.1 Outline flow diagram (Sulphate process)

Drying and Grinding

The raw ore is usually dried and then ground to produce the optimum particle size for efficient dissolution with concentrated sulphuric acid (typically 40-60 μm). Typically ball mills are used for the size reduction process.

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 summarised 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 °C 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, or recycled weak acid. Extreme care has to be taken to ensure that the reaction does not runaway 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. The efficiency of the digestion process is in excess of 95%. Consequently some undigested ore requires separation and disposal.

Reduction

Removal of ferric ions is an essential step, otherwise the ion would remain with the TiO_2 throughout all subsequent processing stages, adversely affecting the quality and colour of the finished TiO_2. This is achieved by contacting the digester liquor with scrap iron to convert all of the ferric (Fe^{3+}) ions to ferrous (Fe^{2+}). The ferrous ion is subsequently very easily washed out of the TiO_2. Normally the reduction process is continued until a small quantity of Ti^{3+} is detected. This stage of process control is essential to maintain product quality.

Clarification and Crystallisation

Any suspended material (e.g. unreacted ore) is removed from the solution by flocculation and filtration. The crude product is washed with water to recover the acid. This weak acid can be either neutralised with limestone before going to landfill, or preferably regenerated and recycled back to the process.

The clarified solution is sent to batch cooler-crystallisers (vacuum) at about 30°C to remove the bulk of the ferrous sulphate as solid (copperas). The copperas crystal is separated by centrifuging and can be used to make ferric sulphate for water treatment, or used in the pharmaceutical and pigment industries. The iron depleted product liquor is polished using candle filters to remove fine particles (to ensure satisfactory colour quality) 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:

$$\mathrm{Ti\,OSO_4 + 2H_2O \rightarrow TiO(OH)_2 + H_2SO_4}$$

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 and either zinc or trivalent titanium is usually added as a reducing agent. The slurry is "leached" at 50^0 C to remove final traces of iron and undergoes final washing and drying. Conditioning agents are added to the resulting pulp at this point, to enhance crystal growth.

The filtrate is strongly acidic and can either be reconcentrated and recycled back to the process or may be neutralised with lime/limestone and the product gypsum sold for wallboard manufacture etc. The target iron concentration in the final product is typically 20 ppm.

Calcination

The calcining stage is also critical to the final product quality. Conditioning chemicals are added to the pulp prior to calcining to assist in the control and development of acceptable product qualities (rutile form, "blue tone" whiteness, pigment durability). Typically calcining occurs in rotary kilns, with the pulp moving under gravity counter currently to the combustion gases. Water and oxides of sulphur are driven from the pulp. The TiO_2 is precipitated in the anatase form and seeding and control of temperature above 850°C are important to the production of the correct rutile crystalline form of the pigment. The kilns are directly fired with oil or gas.

Solids Processing

The resulting solid is cooled, milled, coated micronised (wet milling) and packed. Two stages of milling may be used:

- Dry milling to breakdown agglomerates from calcining process (up to 20 mm) to 75-100 μm;
- Wet milling with steam to achieve fine particles to correct size for optimum pigment properties (0.2 to 0.4 μm).

The TiO_2 particles are coated with other oxides (e.g. 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).

Materials Balance

A simplified mass balance for the sulphate process is given in Table 5.2. This is based on the production from ilmenite.

Table 5.2: Typical by-product streams in tonne per annum

Ore	Ilmenite (45% TiO_2)
Ore usage	2.2
Copperas ($FeSO_4.7H_2O$)	0.6
Strong Acid plus Weak Acid	2.1 (as 100% acid)
SOx	0.05

Depending on the raw material quality, the consumption of concentrated sulphuric acid is in the range of 2.4 to 3.5 tonnes per tonne of TiO_2 produced. During processing, some of this sulphuric acid is converted to sulphates (primarily ferrous sulphate) and the rest is obtained as weak sulphuric acid. Minimisation of pollution from the sulphate process requires promoting the use of these streams as by-products, and optimising the recycle of sulphuric acid.

5.2.2 Abatement requirements for the sulphate process

Environmental Releases

The EC Council Directive 92/112/EEC of 15 December 1992 establishes standards for waste from the titanium dioxide industry. Acceptable releases for the sulphate process are given in Table 5.3

Table 5.3: EC release limits for the sulphate process

Waste	Permit Limit
Strong Acid Waste	None permitted
Solid Waste	None permitted
Weak Acid plus Neutralised Waste	800 kg SO_4/te TiO_2*
SOx	10 kg/te TiO_2
Dust - Major	50 kg/Nm^3
- Minor	150 kg/Nm^3

* Interim limit 1200 kg SO_4/te TiO_2

Within the directive the wastes are defined as:

Solid Waste - (a) insoluble ore residues not broken down by sulphuric acid during the manufacturing process or (b) copperas i.e. crystalline ferrous sulphate ($FeSO_4.7H_2O$).

Strong Acid Waste - mother liquors from the filtration following the hydrolysis stage.

Weak Acid Waste - wash waters etc. containing 0.5% or less sulphuric acid.

Neutralised Waste - any liquid (with pH over 5.5), containing traces of heavy metals, obtained from acid wastes after neutralisation.

Review of Best Practicable Environmental Option (BPEO)

Feedstock options for the sulphate process are either ilmenite ore (45-60% TiO_2) or a titanium-rich slag (70-85% TiO_2). Clearly, the less pure feedstocks will tend to result in the higher production of by-products such as insoluble ore residues and copperas solids, and higher consumption of sulphuric acid per tonne of TiO_2 product. BPEO would therefore be to utilise a feedstock with the highest practicable TiO_2 content. For a given feedstock, appropriate abatement techniques must be utilised to ensure compliance with the EC Directive. It is understood that some sulphate plants in Germany are limited to waste levels in "weak acid waste plus neutralised waste" of 500 kg SO_4/ te TiO_2 which is less than the limit of 800 kg SO_4/ te TiO_2 in the EC Directive. These levels can be achieved by extensive recovery techniques to maximise sulphur values.

Review of Abatement Techniques

The spent sulphuric acid solutions from TiO_2 production are typically of the following composition: 18-25% H_2SO_4, 10-18% $FeSO_4$ and 3-5% other sulphates including $TiOSO_4$, $MgSO_4$, $Al_2 (SO_4)_3$, $CaSO_4$ and others. The correct control of the TiO_2 filtration and washing process and the correct choice of filter allows a considerable reduction in waste solution and the separation of the concentrated solution fraction (22-25% H_2SO_4) which may be utilised effectively after concentration. 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 includes: -

- Conversion of ferrous sulphate to the ferric form, which is used in water treatment.
- Regeneration of spent strong acid or treatment of the spent strong acid to produce white gypsum (for wallboards) and red gypsum (agricultural use). A high quality CO_2 is produced during gypsum manufacture. This may be bottled and sold for carbonated drinks.
- Recycle of the spent weak acid to aid dissolution of the digested titanyl sulphate or neutralisation.
- Abatement of oxides of sulphur releases resulting from reaction of the ore with sulphuric acid (as described in Section 2).

- Minimisation of particulate emissions by conventional techniques.

Specific abatement techniques for the sulphate process are described more fully below.

(a) Ferrous Sulphate Separation From Waste Acid Solutions

Recovery of the hydrated sulphate $FeSO_4.7H_2O$ from the spent solutions is achieved by crystallisation. The crystallisation is carried out by cooling the solution to 0-10°C, for example in a vacuum crystalliser, or by cooling the solution with brine and centrifuging the crystallised salt. The solubility of ferrous sulphate in 20-25% sulphuric acid solutions at a temperature of 0-10°C is 4-6%. It is thus possible to reduce the $FeSO_4$ concentration by nearly 50% by cooling the solution. The product obtained is of commercial quality and can be used in ferric pigment production, water and sewage treatment, special mineral fertilizers, fodder mixtures for stock etc.

Demand for ferrous sulphate, however, is limited and is largely satisfied by iron metallurgy (wastes generated by metallurgical etching). Sulphuric acid solution after a partial crystallisation of $FeSO_4.7H_2O$, (H_2SO_4 concentration rises by 3-5% upon removal of the water of crystallisation) may be partly recycled to the process.

(b) Reconcentration and Recycling of the Acid

The strong acids may be reconcentrated to 65-70% and, if necessary, to levels in excess of 90%. Concentration involves precipitation of the sulphates, particularly the iron sulphates. The first difficulty is to filter the sulphates followed by their treatment otherwise they cannot be stored. Treatment includes destruction of contaminants by roasting and subsequent recovery of SO_2 or by neutralisation.

Recycling the acid used in the manufacture of titanium dioxide is more complicated because of the quality requirements for such production. The acid recovered may be mixed with fresh acid for leaching, provided the mixture is sufficiently strong. This depends on the ore that is used, since slags, which are less reactive, need stronger acid. In particular, plants operating with slag must concentrate the acid from 70 to at least 90% and/or provide for the addition of oleum. Aluminium oxides in the slag also cut down the acid yield from filtration.

- The main problems which had to be solved in recycling the sulphuric acid included:-
- The aggressive and strongly corrosive effect of diluted H_2SO_4 on the majority of commonly used construction materials, especially at higher temperatures;
- The high consumption of energy for evaporation of the very dilute solutions;
- The size of the installation necessary for the utilisation of TiO_2 production wastes;

- The high concentration in the solutions of salts, with a negative temperature coefficient of solubility and the salting out effect of concentrated H_2SO_4 (30-40% H_2SO_4), causing precipitation of the salts during concentration and scaling of the heat exchanger surface;

- The high contamination of the concentrated solution with dissolved salts and suspensions difficult to remove by conventional methods;

- The dependence of TiO_2 production continuity on the efficiency of the concentrating installation in the event of a lack of other solutions for waste removal;

- The need to remove or utilise salts precipitated during concentration, and the removal of impurities to give acid of adequate purity for pigment production.

The capital costs of sulphuric acid concentration and purification installations are assumed at 15-20% of the erection cost of a TiO_2 production plant, whereas their operating costs amount to 10-15% of pigment production costs. It is possible,using a concentration process, to recirculate the 50-70% H_2SO_4 solution to the titanium ore digestion process.

The process leads to excess acid because of the need to add pyrites or sulphur to the metallic salts during the roasting. It generates solid residues which are difficult to use and may therefore necessitate landfill. It presents technological difficulties such as problems of reliability and corrosion. The techniques of concentration by evaporation involve a number of stages, including a major stage at around 65%, at which almost all of the iron sulphate precipitates in the form of monohydrate. This may create scaling and equipment blockages. The need for continuous operation may require parallel use of two treatment units and the installation of intermediate storage, if the problem of maintenance stoppages is to be avoided.

One variant of the procedure would be to neutralise the metallic salts, but this entails the loss of large quantities of acid during filtration and also raises the problem of disposal of the neutralised sludge.

(c) Production of Gypsum

Waste solutions from TiO_2 production may be neutralised in a single stage with limestone, or in two stages with limestone and calcium oxide (milk of lime). In the former, only free sulphuric acid is neutralised, and in the latter, hydrated oxides (hydroxides) of transition metals are precipitated. The two-stage process leads to the formation of two basic grades of gypsum. The first grade (white gypsum) is suitable for use as a building material (wall board); the second grade contains other sulphates e.g. iron, magnesium and has been referred to as red gypsum. It is suitable for conditioning of agricultural land.

Since the waste solutions contain on average 20% of free sulphuric acid and 10-12% of transition metal and alkaline earth metal sulphates (Mg, Ca), the complete neutralisation of 1 tonne of the solution requires approximately 210 kg $CaCO_3$ or 53.5 kg $Ca(OH)_2$. For a 100 te TiO_2 per day, ca 600 te/day of gypsum will be formed; requiring 2.75 tonnes of lime /1 tonne of TiO_2.

Limestone, dolomite, lime or calcium hydroxide (hydrated lime) may be used for the neutralisation of spent sulphuric acid solutions. Since neutralisation gives rise to the formation of almost insoluble calcium sulphate, a film is deposited on the surface of the calcium carbonate particles inhibiting the neutralisation process. In order to achieve a high degree of $CaCO_3$ reaction, limestone of 20 mesh grain size should be used in the neutralisation. Natural limestone contains 80-90% $CaCO_3$. In practice, during neutralisation of concentrated spent sulphuric acid solutions from TiO_2 production, about 3 tonne gypsum per 1 tonne of TiO_2 is obtained. The gypsum suspension is usually separated by filtration for subsequent conventional treatment for producing building materials.

An alternative use, where there is restricted demand for building products, is in cement clinker production. Application of either method of waste minimisation may provide additional sales value for TiO_2 production. Carbon dioxide is formed during the gypsum manufacturing process. As it has sales value as food grade, it is considered to be a useful co-product.

(d) Abatement of weak acid

The chalk or lime neutralisation process for sulphuric acid and metallic sulphates is well known and relatively straightforward. It generates a very large amount of secondary effluent (gypsum and neutral liquid waste). It can be practical, however to re-use the acid, either for:-

- dissolution of the titanyl sulphate cake;
- transfer of the slurry to the gypsum process; or
- use as a co-product for minerals extraction, for example mines tailings.

(e) Alternative co-products

Neutralisation processes may be used to produce other useful mineral by-products. Amongst preferable potential utilisation methods, the following should be emphasised:

- Calcination of $FeSO_4$ and thermal decomposition of the sulphate
- The production of iron pigments, mainly for civil engineering purposes; and
- The production of K_2SO_4 and iron oxides by conversion of $FeSO_4$ with KCl and ammonia.

The $FeSO_{4/}$ salt calcination process involves decomposition in a fluidised bed at about 1000^0C. The energy needed for this purpose is provided by burning pyrites and coal. The SO_2 obtained in this way is purified and cooled in a plant of the type used in the roasting of pyrites and then passed to a double contact plant in which it is converted into sulphuric acid and/or oleum.

5.2.3 Potential release routes

Releases to air

- Oxides of sulphur from digester.
- Oxides of sulphur from kilns.
- Oxides of carbon from kilns.
- Particulate matter from kilns 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.

5.3 Chloride Process

5.3.1 Process Description

Feedstock

An outline flow diagram is shown in Figure 5.2. 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, since impurities, such as iron in the ore feed, result in a net loss of chlorine. Significant quantities of make-up gas are required. There are some restrictions placed on the feedstocks; for example, high levels of manganese and alkaline earths are not acceptable.

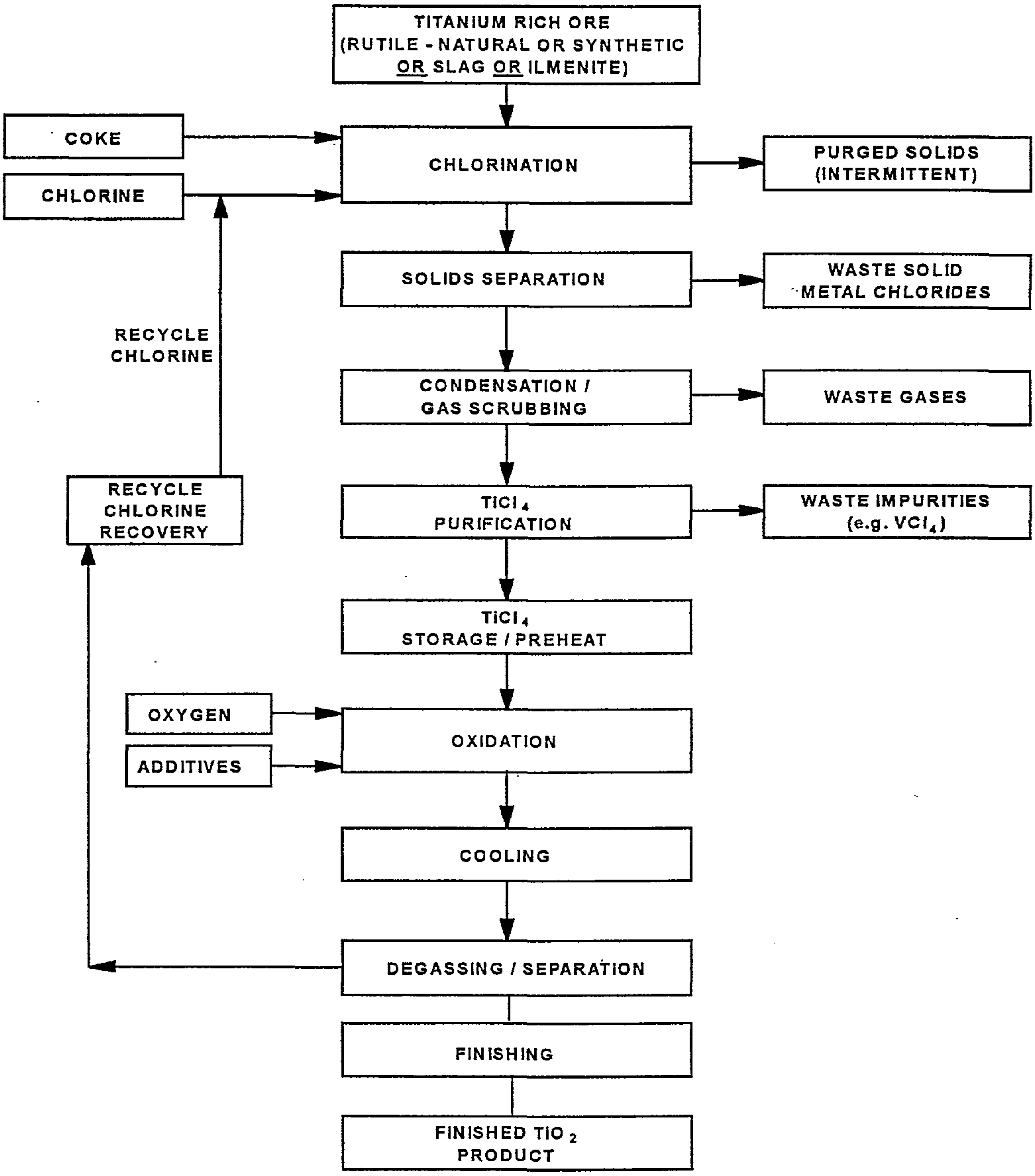

Figure 5.2 : Outline Flow Diagram (Chloride process)

Reaction

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

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

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/carryover 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. Certain metal chlorides (e.g. magnesium and calcium) also accumulate in the fluidised bed reactor due to their low volatility.

All other constituents of the raw materials are volatilised as chlorides in the reactor gases. The chlorination exit gases comprise titanium tetrachloride, carbon monoxide, carbon dioxide, and impurity metal chlorides/oxychlorides.

Purification of Crude $TiCl_4$

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 condensation/gas scrubbing of the $TiCl_4$ stream removes more impurities and the crude $TiCl_4$ then passes to primary purification/distillation where remaining impurities are reduced to very low levels.

Oxidation

Oxidation of the $TiCl_4$ to titanium dioxide and chlorine is carried out at between 1000°C 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. In paticular additives are added to initiate crystal nucleation/growth. The oxidation products are a mixture of chlorine and oxygen gases and titanium dioxide powder. The powder is separated using, typically, bag filters.

Quenching and finishing

The product stream is quenched after exiting the reactor, normally by indirect water cooling. The TiO_2 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 recovery

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.

(1) Absorption/ Desorption

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.

(2) 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. The hot gas stream is cooled, and the solid TiO_2 phase is separated from the chlorine rich gaseous phase. Recycle chlorine is recovered and is recycled to the chlorination process, typically via a liquefaction unit. The chlorine adsorbed on the TiO_2 particles can be removed by heating or by flushing with nitrogen or air. The solid TiO_2 particles are then ground, surface coated and packed.

Materials Balance

In the chloride process utilising rutile ore feedstock, typical material balances for TiO_2 pigment from the rutile and blended feedstocks are illustrated in Table 5.4.

Table 5.4: Typical material balance tonne/tonne of TiO_2 produced

Ore (composition)	Rutile (95%TiO_2)	Mixed Ore (70%TiO_2)
Ore usage	1.1 to 1.2	1.4 to 1.6
Chlorine	0.1 to 0.2	0.6 to 1.2
Coke	0.1 to 0.2	0.15 to 0.25
Oxygen	0.4 to 0.5	0.4 to 0.5
Waste Solid Metal Chlorides	0.1	0.5

As shown in the table, the lower the TiO_2 content of the feedstock (e.g. 70% TiO_2, for a mixture of ilmenite, leucoxene and rutile ores), the greater is the impact on plant capacity. Feedstock demand is higher, metal chloride by-products increase, chlorine and coke consumption increase to achieve the same $TiCl_4/TiO_2$ output. In consequence, capacities of the chlorination, separation and purification equipment must be increased.

Most of the chlorine used is recycled, but a large amount of make-up chlorine is still required to account for metal chloride losses. Oxygen consumption is high, requiring access to local supplies or on-site production (through air separation).

5.3.2 Abatement requirements for the chloride process.

Environmental Releases

The EC Council Directive 92/112/EEC of 15 December 1992 establishes standards for waste from the titanium dioxide industry. For the chloride process, the standards are shown in Table 5.5.

Table 5.5: European Union permit limits

Waste	Permit Limit
Strong Acid Waste	None permitted
Solid Waste	None permitted
Weak Acid Plus Neutralised Waste	130-450 kg Cl/tonne TiO_2 (depends on feedstock)
Chlorine	5 mg/Nm^3 (average) 40 mg/Nm^3 (inst.)
Dust - Major	50 mg/Nm^3
- Minor	150 mg/Nm^3

Within the directive the wastes are defined as:-

Solid Waste

(a) Insoluble ore residues not broken down by chlorine in the manufacturing process.

(b) Metal chlorides and metal hydroxides (filtration substances) arising in solid form from the manufacture of $TiCl_4$.

(c) Coke residues arising from the manufacture of $TiCl_4$.

Strong Acid Waste means waste containing more than 0.5% free hydrochloric acid.
Weak Acid Waste means wash waters etc. containing 0.5% or less free hydrochloric acid.
Neutralised Waste means any liquid (with pH over 5.5) containing only traces of heavy metals, obtained from acid wastes after neutralisation.

Review of BPEO

Feedstock options for the chloride process are much more flexible than for the sulphate process.

The chloride process can process the expensive high titanium content feedstocks, such as rutile ore or synthetic rutile, which result in much less production of wasteful metal chloride by-products, and less consumption of chlorine and coke. BPEO therefore is for a plant to utilise a feedstock with the highest economically justifiable TiO_2 content eg rutile with 95% TiO_2. In addition, the chloride process can attack certain feedstocks, which are not suitable for the sulphate process.

For a given feedstock, appropriate abatement techniques must be used for releases to air, water and land to ensure compliance with the EC Directive. The major difficulty for the chloride process is disposal of the waste solids from the chlorination stage and from the $TiCl_4$ purification stage. The waste solids consist generally of metal chlorides, and the solubility of metal chlorides creates problems with the land disposal of such wastes, as even after neutralisation the chloride ions remain highly soluble. The best option for disposal of such metal chlorides would be further processing to recover (and if possible recycle) the chlorine values and/or to convert the metal chlorides into substances which can be sold and utilised, rather than being used as landfill.

Review of Abatement Techniques

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 in the UK to convert carbon monoxide in the tail gas to carbon dioxide, which reduces the toxicity of the discharge gases.

Liquids

Metal chlorides from the reaction stage may be converted 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 in a waste heat boiler. The process allows for recovery of the chlorine content of the wastes as hydrochloric acid (and hence chlorine value) if the acid is sold, not neutralised.

Solids

Waste solids from the chlorination stage, include metal chlorides (unless roasted , as described above), coke and some ore. These may be neutralised with a wet chalk-lime slurry. The metals are precipitated as hydroxides. The filter cake is land filled and the aqueous filtrate is discharged to a local water course.

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.

Where hydrochloric acid is recovered by roasting the metallic chlorides, a waste oxide solid is produced and is normally land-filled. The process has potential for producing a relatively inert oxide with sales potential (as an inert filler).

5.3.3 Potential release routes

Releases to air

- Carbon monoxide/carbon dioxide tail gas emissions to stack. (The percentage of monoxide to dioxide varies between 20-40%,), unless thermally converted to CO_2

- Hydrogen chloride from absorbers.

- Chlorine from absorbers and storage tanks.

- Titanium tetrachloride from storage vents.

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.

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.

5.4 Comparison between the Sulphate and Chloride Processes

As indicated in section 5.1, there has been a strong trend for plants being built in recent years to use the chloride process. Although the process itself employs more sophisticated process technology than the sulphate process, it is generally preferred, environmentally - producing lower volumes of undesirable effluent materials as well as producing higher performance pigments.

The sulphate process generally produces 8 to 12 te of waste per te of pigment. By comparison, the chloride process generates only 2 to 5 te of waste.

In the sulphate process, impurities are extracted in the form of their sulphates; in the chloride process, in the form of their chlorides. In both instances, the amounts of by-products depend directly on the impurity content of the raw material. The effectiveness of environmental controls depends on how these by-products are dealt with.

The chloride process offers significant technical challenges. For instance, titanium tetrachloride reacts violently and exothermically with water (to give titanium oxychloride and hydrochloric acid). Any small leaks that might occur and vents will produce visible white finely divided plumes of TiO_2, following reaction with water vapour in the atmospheres. Oxidation needs to be carefully controlled and liberated chlorine, which is recycled, is a hazardous chemical.

The chloride route, however has several advantages that favour its use:

- It is a continuous process and is generally less intensive with respect to capital investment, labour, and energy requirements.
- It produces much less waste due to the higher TiO_2 concentration in ore that can be handled.
- It produces superior TiO_2 pigments for high performance applications.

Based on the above review the chloride process may be seen as providing BPEO for TiO_2 production, particularly whilst high concentration ores are available..

Use of the sulphate process is required for the production of anatase, where lower abrasivity and compatibility with optical brighteners are preferred in applications such as certain fine papers. In order to optimize other parameters, the sulphate process does not produce a 100% rutile, and this is a handicap in applications, such as performance coatings, where rutile's characteristics are of value.

North America and Western Europe together account for well over 70% of total effective capacity. Most of North American capacity is based on the chloride process, while in Europe, most of the production is based on the sulphate route. In Asia, most capacity is also based on the sulphate route.

Several factors account for this pattern. In addition to their strict waste disposal rules, US producers enjoy relatively low prices for both energy and chlorine. Until relatively recently, ilmenite was considered an unsuitable feedstock for direct use in the chloride process, mainly because its relatively low TiO_2 content required so much chlorine. However, one US company. began to use a proprietary chloride-based process that uses ilmenite directly as a feedstock, with no pre-processing. The ability to chlorinate relatively low-cost ilmenite provides a cost advantage. The production costs for TiO_2, for this version of the chloride process, were reported to be $297(£180 at $1.65/ £1) per US ton of ilmenite, vs. $531(£322), $539(£327) or $666(£404) respectively, using slag, synthetic rutile and natural rutile. The normal high abatement requirements of "low" grade ores were avoided as the firm was permitted to dispose of the iron chloride waste materials via deep well injection due to pre-existing "grandfather rights ". This method of disposal may not be allowed in the future.

Whilst the ideal raw material is mineral rutile, due to the limited availability of this, few high TiO_2 containing ores are being used. The titanium is usually found in conjunction with iron, and other metals, e.g. V, Nb, Cr. Since chlorination occurs at high temperatures, these other elements are also converted to chlorides and must be separated before oxidation occurs.

It has been claimed that the chloride process is environmentally clean. The disposal of metal chlorides however is a problem to the industry and no clearly preferred commercially viable end-use has been universally established by the TiO_2 industry for these by-products. As TiO_2 values in feedstock ore decline so will the clear-cut environmental and cost advantages of the chloride process. The BPEO situation may not be as clear-cut in future.

6. BEST AVAILABLE TECHNIQUES FOR CONTROLLING RELEASES

6.1 Introduction

This section provides for a review of techniques for controlling releases that are common to many process operations or are considered to be general in their application.

The standard techniques for pollution abatement are outlined in various reference sources including:

- Separation Processes Service, manuals and reports;
- Effluent Processing Club, manuals and reports;
- Air Pollution Advisory and Review Group, reports;
- BAT Review Reports on Pollution Control;
- HMIP Technical Guidance Notes; and
- Environmental Technology Best Practice Programme Guides(ETBPP).

These basic techniques are well established and the purpose of this section is to identify improvements, or clarify particular aspects, of these techniques.

The first stage in minimising releases, howver is through the effective management of the processes to minimise the ultimate release levels.

In this context, there has been growing emphasis on putting into place effective managment systems, which have in recent years covered quality assurance, saftey and environment. International standard ISO 14001 provides guidance for environmental management systems (EMS).

This standard amongst other aspects requires operators to:

- assess environmental impacts of their operations.
- set targets for these impacts that should not be exceeded.
- ensure continuous improvement of the targets.

Whilst ISO 14001 is not the only model for the EMS, it is now internationally recognised.

Systems should be put into place to:

- identify and quantify releases, under normal and credible abnormal events.
- ensure the effectiveness of process operations and controls to minimise releases.
- incorporate suitable abatement systems to mitigate releases.

6.2 Releases into air

6.2.1 General

The aim should be to maximise material recovery, and minimise releases by applying appropriate techniques, including abatement. The principal pollutants to be controlled are NOx, SOx, particulates, and other contaminants. The techniques for abating these releases are well established.

In recent years, focus of concern has been placed on refrigeration materials, due to the problems of ozone depletion. The selection of refrigerant to chill and liquefy gases 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 which 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
- health and safety

6.2.2 Particulate matter

Selection of abatement systems for dust and particulate removal may include the following used on their own or in combination:

- cyclones
- fabric filters
- high efficiency particulate arrestors
- ceramic filters
- wet collection devices
- electrostatic precipitators - both wet and dry
- dust suppression equipment

The appropriate technique depends on the size and other physical and chemical characteristics of the particles, loading, and 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 reused where practicable.

Cyclones

Cyclones are relatively cheap devices for particulates separation. Where high particulate loading is a problem, cyclones can be installed in series to increase the particulate abatement. While cyclones are usually able to deal with high particulate loading they may not be able to provide the level of abatement required especially if small particles are present in the gas stream. In such cases, additional but different type of abatement equipment may be needed downstream of the cyclones.

Fabric filters

Fabric filters are particularly useful as secondary or tertiary gas cleaning devices downstream of a cyclone or dry scrubber and may be enhanced by pre-coating the filter cloth. Apart from limitations of use with respect to moisture-laden streams or those with acidic, tarry or sticky characteristics, there are likely to be temperature limits on fabrics.

Also, regular maintenance and cleaning of the filters is necessary to maintain removal efficiencies and limit pressure drops. Cleaning may be achieved by reverse jet of air, involving the filter to be off line for the cleaning cycle, hence requiring a bank of filters to achieve continuous abatement of particulates.

Ceramic filters

Ceramic filters may block quickly, shown by an increase in pressure drop. Regeneration may howver be achieved by reverse air pulse at about 7 barg; an operation similar to that undertaken with bag filters.

Wet collection devices

One limitaion of wet devices is that, by their very nature they will saturate the gas being cleaned. This will result in a visible water vapour plume, when the gas stream is discharged to air. Reheating of the gas stream may be needed to avoid the vapour plume.

Scrubbers may also produce a liquid effluent that requires treatment. Hence the size and design of the water treatment plant has to be adequate to cope with this discharge.

Electrostatic precipitators

Electrostatic precipitators (ESPs) of the wet or dry type provide very high collection efficiencies of dust or fume particles down to 0.01 micron diameter and may operate at high temperatures (up to 450°C) or high humidity,

The main advantage of the ESP is that it is a low pressure drop device. It is however unsuitable for use where flammable gases may be present: as there may be a sparking off explosions of flammable gas mixtures. This limits the application of electrostatic precipitators 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.

Dust suppression equipment

The storage of dusty materials in stockpiles will require dust suppression. They will need to be kept moist to arrest dust pollution. Sometimes a silicon spray may be utilised to suppress the dust.

6.2.3 Gaseous abatement techniques

Since most of the gaseous pollutants covered in this report are capable of being absorbed in a suitable medium, this part of the BAT review is limited to the absorption processes.

Absorption

General

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.

In wet 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 BPEO, since the absorption process may concentrate the pollutant into the absorbent and may make recovery for re-use or sale, or treatment easier.

Spray towers

Spray towers may 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 solid blockage problems.

Spray towers or spray driers 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.

6.2.4 Chimney and Vent plumes

Chimneys and vents are used to for the final release of gaseous pollutants and represent the final stage of abatement. It is essential that the final releases are at a sufficient elevationto achieve adequate dispersion of pollutants.

Air dispersion models are frequently used to assess the adequacy of proposed stack and vent heights. Operators will normally need to use computer based dispersion modelling software to take account of local meteorological data, local topography and structures, and other local releases.

The operator should make allowance for start up and turn down conditions as well as possible plant or process malfunctions in determining the stack and vent height.

Monitoring of stack emissions should be conducted and reported in accordance with the I.P.C. authorisation.

6.2.5 Odours

Odorous substances, which are present in emissions to air should be identified and quantified. Techniques should be employed to ensure that releases are minimised to prevent the odours being noticeable outside the site boundary. Carbon adsorption and other types of odour adsorbing material may be utilised.

6.3 Releases into water

6.3.1 General

Aqueous wastes may contain dissolved heavy metal compounds including sulphates and fluorides as well as suspended solids. Several well established techniques are available and described in detail in various guidance notes. Techniques that should also be noted are:

- Use of energy conservation methods, including improved control and optimisation of operating conditions.
- Training of personnel in housekeeping techniques, especially in contingency spill procedures to prevent the accidental release of raw materials, products and waste materials into water .

Treatment methods, including combinations of in plant treatment, primary, secondary and tertiary treatment should be applied, as appropriate. Generally the larger the site effluent volume, the more complex will be the treatment system. Smaller sites (less than 40m^3/day effluent) are liable to carry out just 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 precent excursions from being caused by process plant upsets.

(b) Secondary/Tertiary Treatment

The use of reed beds may be an effective method of tertiary treatment.

6.3.2 Membrane processes

Membrane processes include; ultrafiltration, reverse osmosis, membrane filtration, and pervaporation. The efficiency of the filtration processes depend upon the difference in size between the pore and the particle to be removed or retained; whilst in reverse osmosis the efficiency depends on how well the membrane rejects the flow of solute whilst allowing the flow of solvent. This is determined greatly by the amount of solids present in the stream to be cleaned.

These types of process can be used to either clean-up the waste water for recycling, or for recovering 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 operator should demonstrate its suitability and show that the efficiency is at least as good and preferably better than other available techniques.

6.4 Releases to land

One waste material that is often over-looked and requires attention is that of disposal of packaging. It should be reduced to the minimum necessary and will require co-operation with suppliers of products brought onto the site.

7. MONITORING

7.1 General

EA provides series of Technical Guidance Notes on monitoring, containing information on theory and methodology, and providing technical information on monitoring techniques.

Quality assurance procedures should be implemented to ensure that monitoring and test results are sufficiently accurate and reliable (for example by reference to British/ international standards and accreditation with the National Measurement Accreditation Service (NAMAS)).

Requirements and frequency of sampling, analysis and monitoring should be set for a site and/or process (ie. specific). The requirements will be influenced by consideration of the anticipated volume and composition of the waste streams.

7.2 Monitoring Releases to Air

For continuous monitoring, release concentration levels should be given on the basis of 95% of the hourly average readings for each rolling 24 hour period not exceeding the release limit, and the maximum hourly average not exceeding 150% of the limit. 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, measurement or determination of the gas flow will be required. 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; recognising the limitations and accuracy of such monitors. Regular calibration checks should be carried out and documented. When continuous monitoring is not appropriate or available, non-continuous monitoring should be undertaken.

The following factors should be taken into account, when continuous monitoring is required for any given release point:

- 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.

Wherever a combustion process (other than flaring) is used for the destruction of a pollutant, its effectiveness should be demonstrated indirectly by monitoring the temperature and oxygen content of the exhaust gas continuously. 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.

Gaseous releases from gas turbines used for electrical generation or gas compression should be monitored as specified in Chief Inspector's Guidance Note IPR 1/2 (revised 1994).

Monitoring should be undertaken during commissioning, start-up, normal operation, and shut-down wherever pracricable

All final releases to air should be essentially colourless, free from persistent trailing mist or fume and free from droplets.

A short-term monitoring exercise may be implemented when the information available on emissions is not considered sufficient.

7.3 Monitoring Releases to Water

Continuous monitoring and flow proportional sampling for releases to water are to be used in preference to other methods. The use of a fixed interval or time proportional sampler for flow rates of less than 1 litre per second may however 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:

- flow rate,
- pH,
- temperature,
- TOC (surrogate for COD/BOD).

Samples should also be monitored for appropriate other parameters such as those given below, over relevant time periods, typically daily, weekly or monthly depending on the circumstances:

- COD,
- BOD,
- hydrocarbon oil,
- ammoniacal and total nitrogen,
- suspended solids,
- phenols,
- sulphides,
- dissolved oxygen (where justified by the nature of the receiving water),
- metals (typically Cd, Hg, Cr, Ni, Zn, Cu, As).

In addition to the regular monitoring carried out to demonstrate compliance with the release limits set, a fuller analysis should be 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 more understanding of the performance of an ETPis required , a short-term monitoring exercise may established to provide information about inputs to the ETP.

7.4 Monitoring Releases to Land

The EA should be advised of the quantity and composition (including prescribed substances) of waste released to land. In addition, written procedures should exist 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. The 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.

7.5 Records and Reporting

The instructions given with the IPC standard authorisation format should be taken into account on:

- reporting and monitoring, and
- records and notifications related to incidents,

7.6 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. The extent to which process releases have been rendered harmless should be assessed and a decision made as to whether environmental monitoring will be necessary. For all 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. Monitoring that is appropriate for the quantity and form of the releases and for the site's location should be selected. 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.

8. ECONOMIC CONSIDERATIONS

8.1 Introduction

In granting a particular site authorisation to operate, the Environment Agency needs to translate the Best Available Technique(s) (BAT) for abatement of releases into site specific Best Available Techniques not Entailing Excessive Cost (BATNEEC). The operator should construct a BATNEEC case in its application, after examining the range of technically feasible process and/or abatement options. Excessive costs are viewed in the context of the process and the industry concerned. The costs of controlling releases should not be disproportionate to the environmental benefits delivered.

In this section, therefore, a review of the assessment of the economic and financial climate and status of the inorganic chemicals industry, as at 1998, has been undertaken (Section 8.2). The economics of key processes have also been assessed using data available in technical journals such as the Stamford Research Institutes' Process Economics Reports (Section 8.3). The data have been updated to a 1998 basis and interpreted for UK investments. Section 8.4 contains information and costs of abatement techniques against which the application of BAT and BATNEEC may be judged.

8.2 The UK Inorganic Chemical Industry Structure and Market

8.2.1 UK Inorganic Chemical Sector as a Whole

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, e.g. plastics and pharmaceuticals. Figure 8.1 shows how both the inorganic and fertiliser chemical output 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.

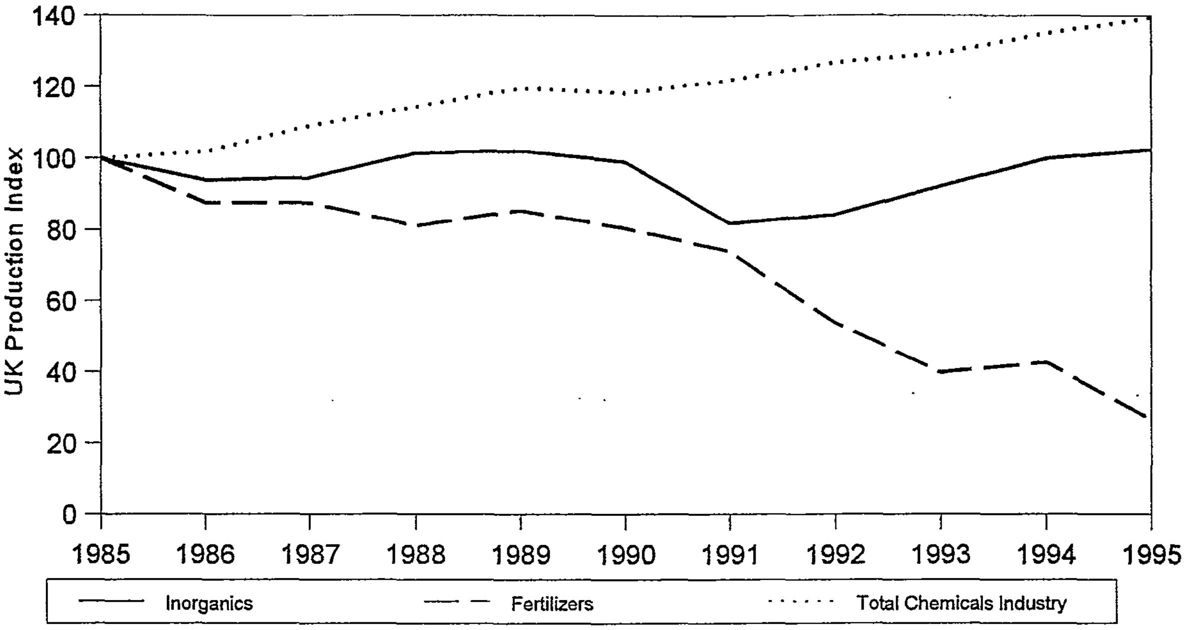

Figure 8.1 UK Production of inorganics, fertilizers and all chemicals

In the last five years there have been major changes in the structure and ownership of the UK and international chemical industry. As an example, a major chemical company is in the process of selling off most of its industrial/commodity chemical activities and acquiring specialist chemical operations. This is probably the biggest structural change in the UK chemical industry since the 1920's. 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.

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 west European chemical industry were in 1989 and 1995 so the cycle lasted six years. The average profit margin (pre-tax profits on sales) for west European chemical companies throughout the last chemical-business cycle was between 2-5% of sales value (turnover) according to a major UK chemical manufacturer.

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 anytime irrespective of the general chemical industry cycle. Examples of these are sulphites, iodates, oleum.

Growth Chemicals

Growth chemicals, for example 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.

Mature Chemicals

Mature chemicals, for example ferric chloride and sodium hypochlorite, are those for which demand is either falling in volume terms or where growth does not exceed 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.

Financial

All companies operating in these industries are public or private limited companies returning annual accounts to Companies House. Important financial ratios which 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.

- The Return on Investment (R.O.I.) is applied to an individual manufacturing plant and is its annual profit expressed as a percentage of the plant investment cost. This simple R.O.I. therefore requires estimates or data for, product selling price, feedstock costs, plant investment costs and operating costs. R.O.I. 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 R.O.I. 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.

Economic Outlook

For each industry sub-sector 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 sub-sectors has been reasonably good by historical standards. This is expected to continue until the next cyclical downturn in the chemicals industry.

8.2.2 Sulphuric Acid and Related Industries

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 1980's 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.

Reported Prices

From the information available, it would appear that fluctuations in both feedstock and product prices have had only minor impact on the overall profitability of the sulphur industry in recent years.

Financial Results

Recent financial results for a typical sulphur-based inorganic-chemical company are shown in figure 8.2. The trend of all four financial parameters appear to track the overall UK chemical-industry business cycle, i.e. recession in the early 1990's, 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.

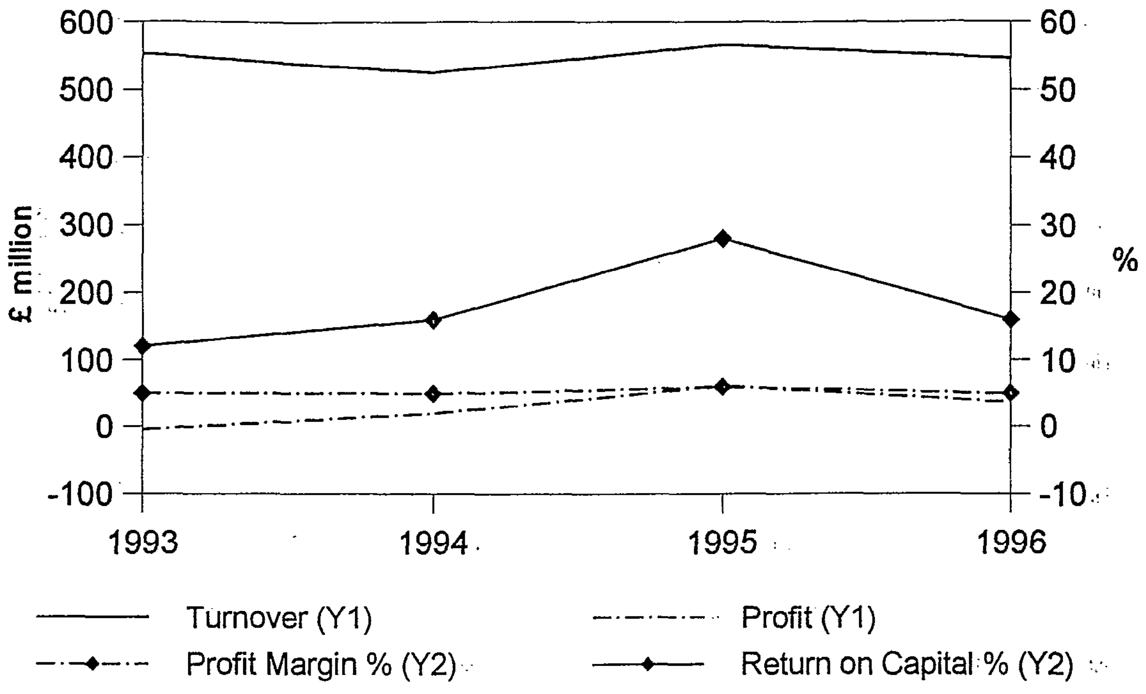

Figure 8.2 Typical financial results for inorganic sulphur-related manufacturers

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.

8.2.3 Nitric Acid and Related Industries

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 acids 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

West European fertiliser production and consumption has declined by about 25% since the end of the 1980's. The markets suffered a disastrous slump in 1991-2. West European demand was declining slowly but, following the breakup 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 incurring 50% redundancy in the workforce.

Now the European fertiliser environment is stabilising and the oversupply situation is improving.

Chemical Markets

Demand for concentrated nitric acid for high-growth chemical production is generally increasing.

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.

Financial Results

Recent financial results for a typical nitrogen-based inorganic-chemical company are shown in figure 8.3. The trends show that losses in 1993 have been turned into profits in recent years up to the start of 1998.

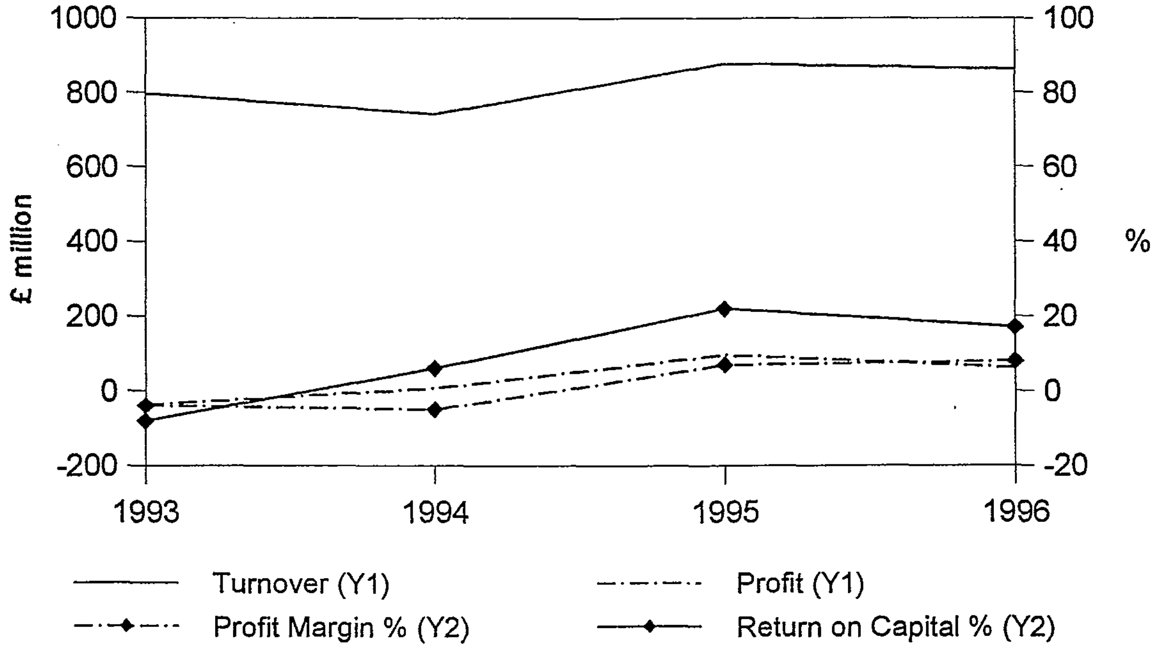

Figure 8.3 Typical financial results for inorganic nitrogen-related manufacturers

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 the early 1990's, 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 consultant's 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.

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 1990's, the outlook for European fertiliser producers has improved.

Positive features are the reduction in EU set-aside land, recovery in domestic demand in east Europe/FSU and the near total lack of investment for 10 years which has helped to reduce over-capacity. 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 east 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.

8.2.4 Inorganic Halogens Industries

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 deregulation and privatisation of the gas supply and electricity supply industries. 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 deadline to phase out the 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 (e.g. over £200 million).

Other Chlorine-Related Markets

Chlorine and ethylene are used to make 'VCM' (vinyl chloride monomer) which is converted into PVC. PVC is the single biggest end use for chlorine but is under environmental pressure to be substituted by other plastics. 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 byproduct 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 byproduct 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 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 byproduct 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.

Methyl chloride is a major feedstock in the manufacture of silicon based polymers which are high growth products in the UK.

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.

Financial Results

Recent financial results for a typical chlorine-based inorganic-chemical company are shown in figure 8.4. 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.

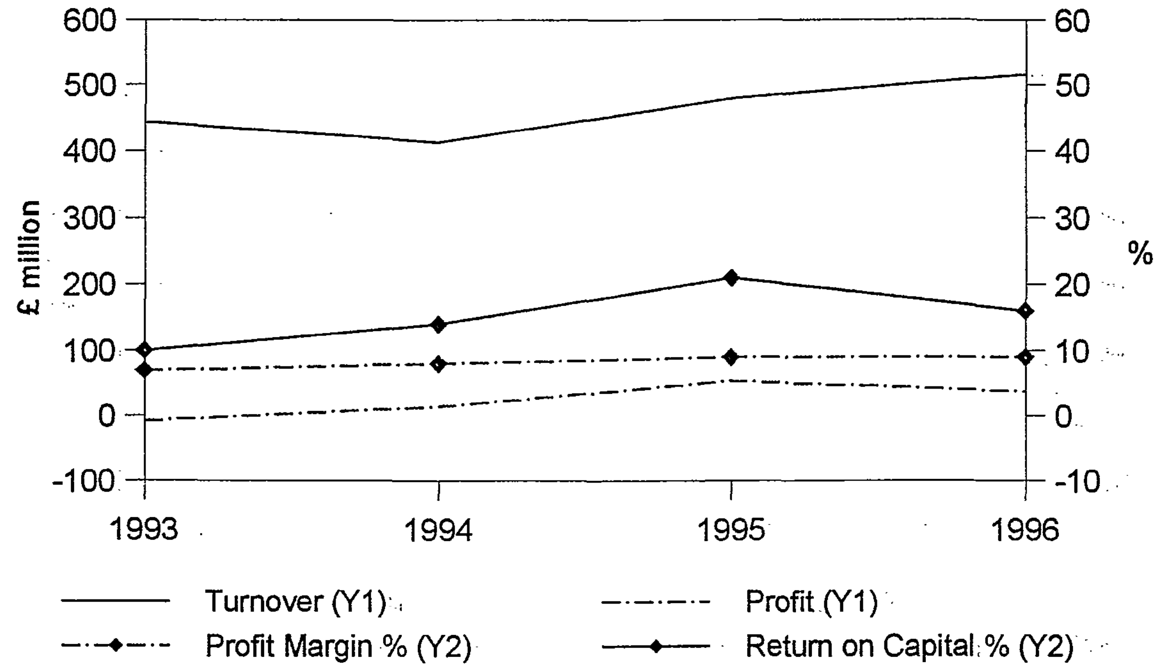

Figure 8.4: Inorganic chlorine-related manufacturers - typical financial results

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. Due 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.

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 west European and UK 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, e.g. 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, e.g. for titanium dioxide, phosgene, 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.

8.2.5 Inorganic Bromine/Fluorine/Iodine Related Industries

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-size manufacturers in each sector in the UK.

Bromine

Bromine is produced from seawater 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 ultra-high purity chemicals. The company is also the world's largest producer of potassium fluoroborate and potassium fluoro titanate 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.

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.

Financial Results

Recent financial results for bromine, fluorine and iodine-based inorganic chemical companies are shown in figure 8.5. 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.

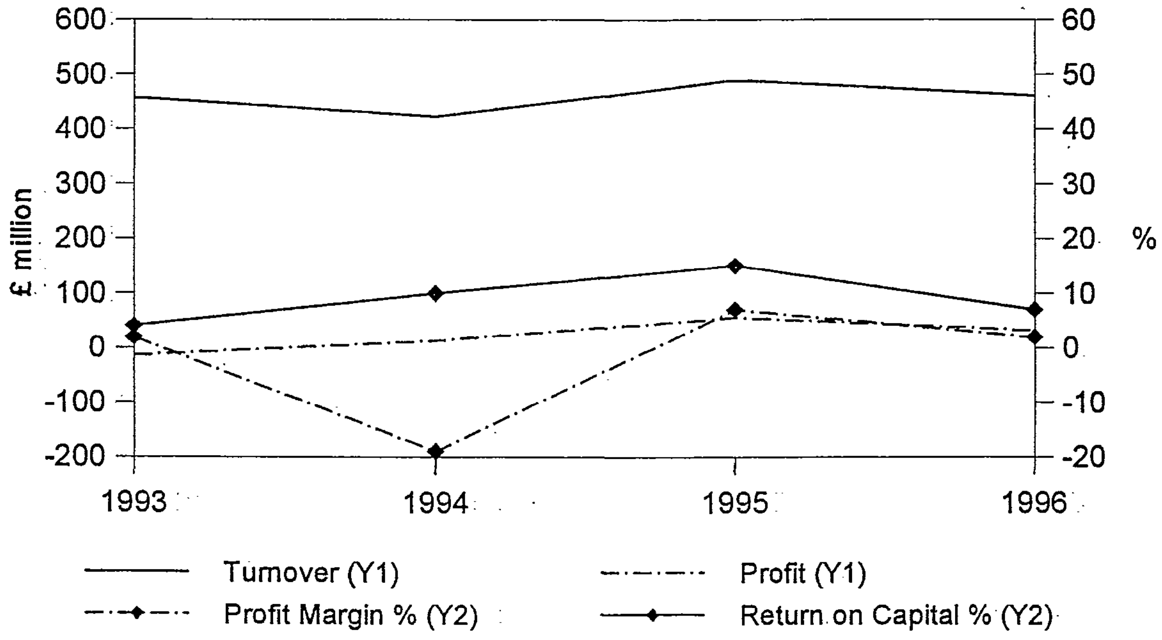

Figure 8.5: Typical financial results Inorganic bromine / fluorine / iodine-related manufacturers

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.

Economic Outlook

Despite the speciality nature of the chemicals produced in this sub-sector, any high prices achieved do not appear to be reflected in the financial results of a typical company.

8.2.6 Titanium Dioxide Industry

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 1980's led to major new- plant investment which resulted in overcapacity, poor markets and lower profitability in the recession in the of the early 1990's. 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 most investment in Europe has been for debottlenecking 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 ‘softer’ toned pigment. For sulphate producers, the markets for byproduct materials (e.g. ferric sulphate and gypsum) can be economically important.

Reported Prices

Titanium dioxide prices improved in 1996, languished in early 1997 and recovered after expansion plans were delayed. Recent titanium dioxide prices have tended to be higher on a historical basis with values close to $1 per lb.

Financial Results

Recent financial results for a typical titanium dioxide company is shown in figure 8.6.

The decline in return on capital in 1996 relates to just one specific result and is probably unrepresentative of the typical economic performance of the sector. The result also covers products other than titanium dioxide and an accurate trend might be difficult to predict.

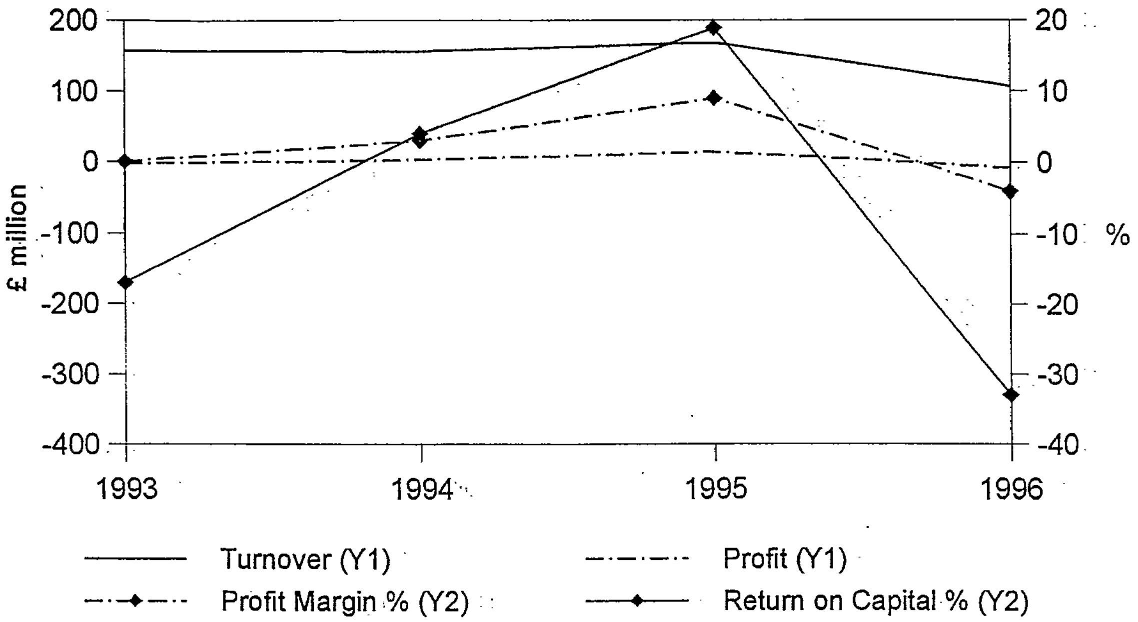

Figure 8.6: Typical financial results for inorganic titanium dioxide-related manufacturers

Current returns on investment for typical titanium dioxide plants (100 ktpa capacity), based on production costs provided by a producer, are estimated to be 31.3% for the chloride route and 24.2% for the sulphate route. The sulphate process appears to be profitable, particularly when using a relatively high titanium dioxide content feed, but the chloride process appears overall to be the more economic process, 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.

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.

8.3 Process Economics

8.3.1 Estimates of Profit Margins

Before tax returns on investment (BTROI) have been estimated for a number of typical new plants, for which the necessary data is available from published non-confidential sources.

The typical plants selected are as follows:

- Sulphuric Acid (93 wt% solution).
- Nitric Acid (60% solution).
- Titanium Dioxide (both processes).
- Chlorine (Electrolysis with Membrane Cells).
- Hydrogen Chloride (anhydrous).
- Phosgene.

These estimates thus cover both the major inorganic acids and certain of the halogens which were the subject of this review.

8.3.2 Method

Investment Cost

Generally battery limit and offsites investment costs (for a new plant located on the US Gulf Coast) were obtained from relevant SRI reported data, and then were escalated from the year of the SRI report to a 1998 (1st quarter) basis. These US$ costs were converted to £ sterling at the assumed exchange rate of £1 = $1.65, and related to UK investment location. It is important to note that the data relate to new plant construction only. Improvements to existing processes are not addressed.

Raw Materials and Product Prices

These were obtained from the Chemical Market Reporter publication (19 January 1998 edition) wherever possible. In some cases, prices were not reported in this publication and best estimates had to be made. In the case of the chlorine price, which is relatively high at present, an average price was used for the period 22 January 1996 to 19 January 1998 (i.e. $214/short ton).

Other Operating Costs

Apart from the raw material costs, the other variable and fixed operating costs were based on relevant SRI reported data, and then more escalated from the year of the SRI report to a 1998 (1st quarter) basis. These US $ costs were converted to $ sterling at the assumed exchange rate of £1 = $1.65. (Depreciation changes have been excluded.)

Profit Margin (£/MT)

This is calculated as the difference between the product selling price (£/MT) and the total operating costs, including costs of raw materials. Again, depreciation changes are not considered.

Return on Investment (%)

The before tax return on investment is calculated from the profit margin, the plant capacity and the investment cost (battery limits plus offsites).

8.3.3 Results

Process economics assessments have been prepared for the listed processes in Tables 8.2 to 8.8.

Table 8.1 below shows the key results of these process economics calculations:

Table 8.1 - Summary of process economic assessments for new plant

Product	Plant Capacity MTY	BTROI %
Sulphuric Acid	328 000	20.3
Nitric Acid	172 000	40.4
TiO_2 (Chloride Route)	100 000	31.3
TiO_2 (Sulphate Route)	100 000	24.2
Chlorine (Membrane Cells)	181 400	16.2
Hydrogen Chloride (Anhydride)	20 000	18.0
Phosgene	35 000	218.0

8.3.4 Conclusions

Sulphuric Acid

Sulphuric acid produced by the sulphur combustion process shows an acceptable BTROI, indicating a reasonable balance in the market for feedstock supply and product demand.

Nitric Acid

Production of nitric acid shows an unexpectedly high BTROI, for the estimated investment cost and profit margin. The relevant SRI report also indicated a very high ROI for the particular process selected, which may well have a technology advantage over older technologies.

Titanium Dioxide

Both process routes have acceptable BTROIs. The sulphate process, with a relatively high TiO_2 content feed, appears to be profitable for new plant construction. The chloride process, however, appears to be more profitable, on the basis used.

Chlorine

Production of chlorine through the membrane cell process shows an acceptable BTROI, but it must be noted that chlorine prices are currently high on a historical basis, and of course the co-product caustic soda price also has a marked effect on the economics of the brine electrolysis process. The investment economics review has been based on the membrane process for the following reasons:

- No new plant investment has been made in Europe, USA or Japan in other technologies (diaphragm and mercury).
- Economic assessments indicate that the membrane process is likely to be as, if not more, economic than other chlorine processes.
- Future trends in regulating requirements are likely to increase abatement costs for the mercury process and, to a lesser extent, the diaphragm process.

Hydrogen Chloride and Phosgene

The anhydrous hydrogen chloride process shows an acceptable BTROI, but the phosgene production process produced an improbably high BTROI figure. This is clearly due to the extremely high reported prices for phosgene of £0.74 per pound, which converts to £995 per metric ton (for 1 ton cylinders). It is probable that bulk prices for phosgene would be significantly lower than these prices reported for 1 ton cylinders.

Table 8.2 - Estimate of profit margins for sulphuric acid (93%)

Process Route	Sulphur Combustion	
Typical plant capacity (tonne/yr)	328 000	
Investment Cost Estimate	**$ million**	**£ million**
Onsite cost	34.0	24.73
Offsite cost	17.4	12.65
Total	51.4	37.38
Operating Costs	**£/te**	
Raw materials	16.7	
Fixed costs	7.1	
Total operating costs	23.8	
Profit Margin	**£/te**	
Selling price	46.9	
Margin	23.1	
Return on Investment		
Before tax return on investment (BTROI = margin x te produced/investment cost (%)		
BTROI	20.27	

Notes:

1. Developed from data in SRI International PEP Yearbook (1988).
2. US prices and costs converted at £1 = $1.65 and US Gulf Coast factors of 1.2.
3. Margin and BTROI figures exclude depreciation charges.

Table 8.3 - Estimate of profit margins for nitric acid

Process Route	Air Oxidation of Ammonia	
Typical plant capacity (tonne/yr)	172 000	
Investment Cost Estimate	**$ million**	**£ million**
Onsite cost	23.4	17.02
Offsite cost	21.8	15.85
Total	45.2	32.87
Operating Costs	**£/te**	
Raw materials	45.2	
Fixed costs	22.0	
Total operating costs	67.3	
Profit Margin	**£/te**	
Selling price	144.5	
Margin	77.2	
Return on Investment		
Before tax return on investment (BTROI = margin x te produced/investment cost (%)		
BTROI	40.39	

Notes:

1. Developed from data in SRI International PEP Yearbook (1988).
2. US prices and costs converted at £1 = $1.65 and US Gulf Coast factors of 1.2.
3. Margin and BTROI figures exclude depreciation charges.

Table 8.4 - Estimate of profit margins for titanium dioxide (chloride route)

Process Route	Chloride Route (Rutile Ore Feed)	
Typical plant capacity (tonne/yr)	100 000	
Investment Cost Estimate	**$ million**	**£ million**
Onsite cost	154	112
Offsite cost	110	80
Total	264	192
Operating Costs	**£/te**	
Raw materials		
Fixed costs		
Total operating costs (see note 4)	800	
Profit Margin	**£/te**	
Selling price	1400	
Margin	600	
Return on Investment		
Before tax return on investment (BTROI = margin x te produced/investment cost (%)		
BTROI	31.3	

Notes:

1. Developed from data in SRI International PEP Yearbook (1988).
2. US prices converted at £1 = $1.65 and US Gulf Coast factors of 1.2.
3. Margin and BTROI figures exclude depreciation charges.
4. Operating costs have been provided by a producer, following discussions on performance and may reflect economies made in recent years.

Table 8.5 - Estimate of profit margins for titanium dioxide (sulphate route)

Process Route	Sulphate Process (for high titanium dioxide feeds eg Ilmenite Slag at 85% TiO_2)	
Typical plant capacity (tonne/yr)	100 000	
Investment Cost Estimate	**$ million**	**£ million**
Onsite cost	276	201
Offsite cost	65	47
Total	341	248
Operating Costs	**£/te**	
Raw materials		
Fixed costs		
Total operating costs (see note 5)	800	
Profit Margin	**£/te**	
Selling price	1400	
Margin	600	
Return on Investment		
Before tax return on investment (BTROI = margin x te produced/investment cost (%)		
BTROI	24.2	

Notes:

1. Developed from data in SRI International PEP Yearbook (1988).
2. US prices converted at £1 = $1.65 and US Gulf Coast factors of 1.2.
3. Margin and BTROI figures exclude depreciation charges.
4. Assumes feedstock cost of £110/Mt.
5. Operating costs have been provided by a producer, following discussions on performance and may reflect economies made in recent years.

Table 8.6 - Estimate of profit margins for chlorine

Process Route	Electrolysis of Brine (Membrane Cells)	
Typical plant capacity (tonne/yr)	181 400	
Investment Cost Estimate	**$ million**	**£ million**
Onsite cost	138.9	101.02
Offsite cost	76.4	55.56
Total	215.3	156.58
Operating Costs	**£/te**	
Raw materials (less soda credit)	-160.4	
Utilities	64.7	
Fixed and variable costs	96.3	
Total operating costs	0.6	
Profit Margin	**£/te**	
Selling price	140	
Margin	139.4	
Return on Investment		
Before tax return on investment (BTROI = margin x te produced/investment cost (%)		
BTROI	16.15	

Notes:

1. Developed from data in SRI International PEP Yearbook (1988).
2. US prices and costs converted at £1 = $1.65 and US Gulf Coast factors of 1.2.
3. Margin and BTROI figures exclude depreciation charges.

Table 8.7 - Estimate of profit margins for hydrogen chloride

Process Route	Chlorine and Hydrogen = Anhydrous HCl	
Typical plant capacity (tonne/yr)	20 000	
Investment Cost Estimate	**$ million**	**£ million**
Onsite cost	3.8	2.76
Offsite cost	2	1.45
Total	5.8	4.21
Operating Costs	**£/te**	
Raw materials	150.3	
Fixed costs		
Total operating costs	177.1	
Profit Margin	**£/te**	
Selling price	215	
Margin	37.9	
Return on Investment		
Before tax return on investment (BTROI = margin x te produced/investment cost (%)		
BTROI	17.97	

Notes:

1. Developed from data in SRI International PEP Yearbook (1988).
2. US prices and costs converted at £1 = $1.65 and US Gulf Coast factors of 1.2.
3. Margin and BTROI figures exclude depreciation charges.

Table 8.8 - Estimate of profit margins for phosgene

Process Route	Chlorine and Carbon Monoxide	
Typical plant capacity (tonne/yr)	35 000	
Investment Cost Estimate	**$ million**	**£ million**
Onsite cost	11	8.00
Offsite cost	5.6	4.07
Total	16.6	12.07
Operating Costs	**£/te**	
Raw materials	129.6	
Fixed costs	113.3	
Total operating costs	242.9	
Profit Margin	**£/te**	
Selling price	995	
Margin	752.1	
Return on Investment		
Before tax return on investment (BTROI = margin x te produced/investment cost (%)		
BTROI	218.04	

Notes:

1. Developed from data in SRI International PEP Yearbook (1988).
2. US prices and costs converted at £1 = $1.65 and US Gulf Coast factors of 1.2.
3. Margin and BTROI figures exclude depreciation charges.

8.4 Cost of Abatement

8.4.1 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 8.9.

The basis for the table is as follows:

- SO_2 concentration at the inlet to the converter is 10% vol/vol.
- Cost data have been developed for a 1000 tpd sulphuric acid plant.
- Processes considered for abatement are conversion to double absorption, introduction of additional catalyst beds (5 bed), use of "low-bite" catalyst to improve conversion and finally addition of a secondary abatement system for the tail-gas.

Table 8.9 - Cost of abatement for sulphuric acid plant

Process	% Conv'n	kgSO_2/te acid	Cost £/tpd acid
Single Absorption	98	14	0
Double Absorption	99.5	3.3	498
5 bed D.A	99.8	1.5	698
5 bed D.A + low bite	99.9	0.6	822
Extra abatement	99.95	0.3	1070

These results are expressed graphically in figure 8.7. 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 8.9 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 to 99.9% overall conversion.

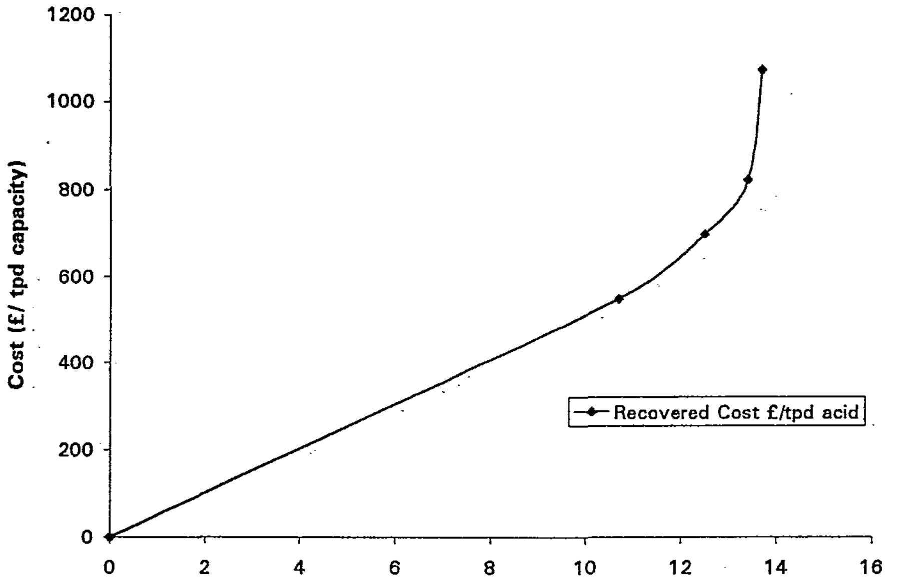

Fig 8.7 SOx abatement costs per tonne recovered

Note: Each point on the curve represents a progression from no abatement to Double Absorption, to extra beds, to low bite catalyst and to extra tail gas abatement (as Table 8.1).

In so far 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 8.9 costs apply to new plant abatement. The use of the same abatement techniques is 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 provide an indication 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.

8.3.2 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 plant, 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 8.10 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 8.10 - Cost of abatement for nitric acid plant

Abatement Method	kg NO_2/te acid	Cost £/ tpd acid
None	9.7	0
EA	0.5	230
EA + SCR	0.15	880
EA + NSCR	0.12	1850

The results are expressed graphically in figure 8.8 in terms of *additional* NO_2 recovery compared with the non-abated process. Two overlapping graphs are shown, providing abatement combinations of either EA with SCR or EA with NSCR. They also show 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 to 99.9% overall conversion.

Note: Two separate, but overlapping curves are displayed, indicating the cost difference between EA/SCR and EA/NSCR (for N_2O Recovery) combinations. The points represent no abatement, use of EA, then use of EA with either NSCR or with SCR.

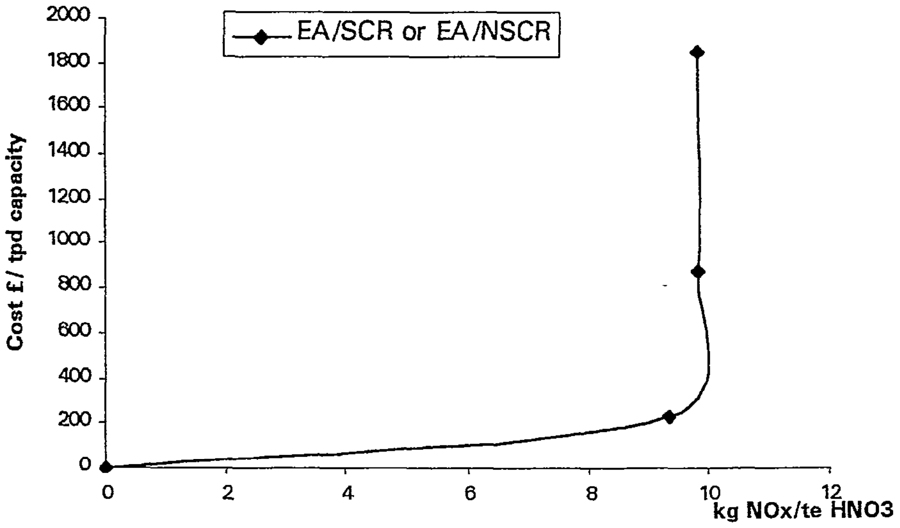

Figure 8.8 NOx Abatement Costs per tonne NOx recovered

In so far as the techniques discussed above are currently commercially available, 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.

8.3.3 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 directive to phase out mercury based processes.

Diaphragm Cells

BAT for asbestos requires compliance with the Asbestos Regulations in terms of safe handling and disposal of spent diaphragms.

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 combination 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.
- Re-design 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 4 "Halogens" and Section 6 "Best available techniques for controlling releases".

8.3.4 Abatement of Titanium Dioxide plant

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).
- Food grade CO_2 for the carbonated drinks market.

The sulphate process also produces weak acid, SO_x, NO_x and particulates from the calcining stage. Provision of BAT is in accordance with recognised techniques that are described in Sections 2.2, 2.3 and 5 of the Guidance Notes and include:

- Abatement for SO_x , NO_X and particulates, arising from fuel firing and calcining.
- Subsequent recovery of the SO_2 generated by the roasting of metal sulphates to make sulphuric acid via the contact process
- Recycling the metal oxides produced by roasting to the steel industry.
- Concentration or regeneration of the spent sulphuric acid for recycle or sale.
- Removal of particulates from the waste gases.

Chloride Process

Tail gases from the chlorination stage of the process contain carbon monoxide, carbon dioxide with some hydrogen chloride and chlorine "slip" from the reaction. Conventional two-stage scrubbing techniques, firstly 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.

9 SUSTAINABLE TECHNOLOGY

9.1 Introduction

Industrial development is a necessary goal of industrialised nations, as societies and people aim to secure higher standards of living. This desire puts pressure on the local and global environment, particularly as societies also desire an acceptable environment, now and for future generations.

Sustainable development and hence sustainable technology is an attempt to reconcile these basic desires. One quoted definition of "sustainable development" from Bruntland is:

> "Development that meets the needs of the present without compromising the ability of future generations to meet their own needs."

Aspects of sustainable development that are being considered by the Environment Agency include:

a. Taking a holistic approach.
b. Taking a long term perspective.
c. Biodiversity.
d. Impact on global atmosphere.
e. Following a precautionary principle.
f. Capability of the environment to accommodate pollutants.
g. Reducing reliance on non-renewable sources, including recycling, resource utilisation efficiency and lifetime availability.

The specific aspects of the industrial processes included in this work scope that impinge on sustainable development are:

1. Raw materials usage, including power/fuel; specifically from non-renewable resources.
2. Impact releases on the local, national and global environment.

The key environmental concerns that industrial developments must now address include global warming potential, ozone depletion potential, low level ozone formation and acid rain.

This section examines the effects that some of the principal industrial processes have on these areas of environmental concern.

9.2 Sulphuric Acid Processes

The raw materials used in most sulphuric acid manufacturing processes consist of elemental sulphur and air. There are also a number of metal extraction processes which use sulphide ores as a feedstock and produce sulphuric acid as a by-product. As a result of the drive to reduce sulphurous emissions from refinery products, there is currently a surplus of elemental sulphur worldwide. It is therefore anticipated that there will be little damage caused to supplies for the foreseeable future. In the long term, however, reliance on excess sulphur production from a non-renewable source (oil sector) will not be sustainable. Sulphuric acid is also formed as a by-product of metallurgical processes. This may be seen as reducing the demand for virgin sulphur and so mitigating the demand for non-renewable sources.

A typical sulphuric acid plant generates steam for export and is not seen as a significant contributor to fuel demand.

The main emissions from the process are unconverted SO_2 emitted in the tail gas from the process; NOx and SOx from the combustion of the sulphur and air; SO_3 and sulphuric acid vapour/mist also from tailgas and from fugitives. These emissions will have little global warming or ozone depleting potential. They will have only a minor effect on low level ozone. They will contribute to acid rain formation, but in comparison with a typical coal fired power station, the contribution will be one to two orders of magnitude less.

Metallurgical processes will also emit small quantities of metals such as mercury, cadmium, zinc, arsenic and lead depending upon which metals are being recovered.

9.3 Nitric Acid Processes

Ammonia and air provide the raw materials for nitric acid process. Ammonia is sourced through hydrogen and nitrogen. In turn the hydrogen, which is the non-renewable raw material is produced by a range of different routes, including hydrocarbon reforming and brine electrolysis (as a co-product of chlorine production). It is therefore considered that nitric acid production is unlikely to have a major impact on these sources.

The nitric acid process is a net producer of energy and has low overall impact on fuel consumption.

The principal emissions from nitric acid processing is NOx, a mixture of oxides of nitrogen. These include N_2O, NO and NO_2 the proportions of which depend on complex interactions. The principal global environmental effect of NO and NO_2 emissions is acidification. It should be noted however that NO_2 contributes to low level ozone formation, although the reactions involved are complex and time dependent. Low level atmospheric reactions of NO and NO_2 with other pollutants, such as VOCs, contribute to adverse effects on low level air quality. Thus release levels are specified for NO and NO_2 and ambient air quality standards have been set. Currently there are no release levels set for N_2O, although it is now recognised as having a significant global warming potential.

Emissions form industrial chemical processes should be seen in context as they contribute about 10% of total NOx emissions to the atmosphere in the UK.

9.4 Halogen Processes

The principal raw materials used in the large scale production of chlorine are brine and electricity. The brine is generally obtained by dissolving salt, usually sodium but sometimes potassium chloride, which is extracted from salt mines in water. The brine is circulated round the process, becomes depleted and the solution is regenerated by adding more salt. As salt reserves are plentiful, and seawater could be used as a replacement, these resources are seen as having long term availability.

Power consumption is however considerable, although it should be noted that the membrane process requires less per tonne of chlorine produced. Energy use should therefore be regarded as non-renewable. A typical figure for a site producing 29 000 tonnes per annum of chlorine using the mercury cell technology is about 0.3 MW/tonne.

The most toxic releases from a chlorine producing process would be mercury, a highly toxic metal which attacks the central nervous system, and asbestos (from the diaphragm process) a significant carcinogen. These emissions are dependent on the level of abatement and the chlorine production process employed. The trend to switch to the membrane process will diminish production of these pollutants.

Emissions to the air which could be converted into acid rain consist only of hydrogen chloride gas which may escape from the hydrochloric acid production process. This gas is readily soluble in atmospheric water and will consequently fall to the ground as a weak acid.

One gas emitted which may have an effect on global warming is carbon dioxide. A typical chlorine plant may generate 0.02 tonne/tonne chlorine. The refrigeration of chlorine involves chlorofluorocarbons (CFCs), which have much higher global warming potential. These refrigerants also have a very significant ozone depletion potential. Alternative refrigerant mediums are being developed.

The main risk to the ozone layer from a chlorine producing plant would be if CFCs were still being used as refrigerants and the container in which they are sealed became compromised either accidentally or during the decommissioning phase of the refrigeration unit.

9.5 Titanium Dioxide Processes

9.5.1 General

Both the sulphate process and the chloride process utilise titanium dioxide ores or synthetic slags as feedstock. The purity of the feedstock is directly related to the wastes produced by the titanium dioxide processes, with higher TiO_2 content being desirable to minimise pollution abatement requirements.

9.5.2 Availability of Feedstock

Naturally Occurring Ores

Large quantities of titanium bearing ores exist in the form of alluvial deposits and hard rocks.

The principal common titaniferous materials are:

Rutile:	Alluvial deposits occurring on or near sea coasts. TiO_2 content about 95%.
Ilmenite:	Massive hard rock deposits (New York State, Southern Norway, Northern Finland and East Quebec). TiO_2 content about 43%.
Ilmenite:	Alluvial deposits, usually on sea coasts in or just outside the tropics. TiO_2 content 55-60%.

Leucoxene: Weathered ilmenite with a TiO_2 content of 65% or above; produced in Western Australia and Florida.

Anatase: Little work on a commercial scale but large deposits exist in Minas Gerais, Brazil.

Whilst ilmenite ores exist in very large deposits, which will meet titanium dioxide demand in the long term, rutile deposits are in short supply. To sustain the industry there will inevitably be a switch to lower TiO_2 ores. However, synthetic slag, produced from other industrial processes, such as iron smelting, is often rich in TiO_2. Typical slags include TiO_2 concentrations in the range 75-90%+. Synthetic rutiles are also available.

Whilst some slags are suitable for use in the sulphate process, most require chlorine for processing. There is therefore likely to be a worldwide shortage of high titanium ore for the sulphate route. The long term trend is likely therefore to favour the chloride process. Here, however, increased chlorine loss is likely as a switch to lower grade ores or synthetic slags is made.

Both processes have a net energy requirement which is non-renewable. The main releases from the sulphate process are spent sulphuric acid and solid wastes such as copperas ($FeSO_4 \cdot 7H_2O$).

The main releases from the chloride process are chlorine, carbon monoxide and dioxide to the atmosphere and metal chlorides into water streams. Small amounts of hydrochloric acid may also be released to the atmosphere. This is readily soluble and may have a localised impact.

The only significant air-borne releases with a long term environmental impact are carbon monoxide and carbon dioxide. The carbon monoxide has a residence time of about 2 years. Assuming 100% conversion to carbon dioxide, total CO_2 equivalent release from the chloride process is about 0.75 tonne CO_2 per tonne titanium dioxide produced. Total release from the UK TiO_2 plants is not significant; equating to less than 0.05% of total anthropogenic releases in the UK.

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ABBREVIATIONS AND DEFINITIONS OF TERMS USED

BAT	Best Available Techniques
BATNEEC	Best Available Techniques Not Entailing Excessive Cost
BPEO	Best Practicable Environmental Option
BOD	Biochemical oxygen demand
CIGN	Chief Inspector's Guidance Note
CO	Carbon monoxide
CO_2	Carbon dioxide
COD	Chemical oxygen demand
DCE	Dichloroethane
DOE	Department of the Environment
EP	Electrostatic precipitator
EPA90	The Environmental Protection Act 1990
ETBPP	Environmental Technology Best Practice Programme
ETP	Effluent treatment plant
g/h	grammes 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
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	All Oxides of nitrogen may be NO, NO_2, N_2O_5 <u>except</u> N_2O
OSPARCOM	Oslo/Paris Conventions for the Prevention of Marine Pollution
PARCOM	Paris Convention
PEP	Process Economics Programme (SRI)
SRI	Stamford Research Insitute
SO_2	Sulphur dioxide
SO_3	Sulphur trioxide
TGN	Technical guidance note
TiO_2	Titanium dioxide
TOC	Total organic carbon
VCM	Vinyl chloride monomer
VOC	Volatile organic compound