COMMISSION OF THE EUROPEAN COMMUNITIES

environment and quality of life

Pollution problems resulting from the manufacture of nitrogenous and phosphate fertilizers

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POLLUTION PROBLEMS RESULTING FROM THE MANUFACTURE OF NITROGENOUS AND PHOSPHATE FERTILIZERS

Final Report

by

L. Whalley

SUMMARY

A survey has been made of the pollution problems which result from the manufacture of fertilizers. The gaseous liquid and solid effluents which arise in each of the unit processes operated by fertilizer manufacturers in the EEC are discussed, together with descriptions of the technology which is available for effluent control. The most important effluents are as follows: In the manufacture of ammonia water pollution can arise from a process condensate containing ammonia, carbon dioxide and methanol. The tail-gas from a nitric acid plant contains nitrogen oxides which are discharged to the atmosphere. Control techniques include the provision of increased absorption capacity, alkaline scrubbing and catalytic reduction of the nitrogen oxides. The tail-gas from a sulphuric acid plant contains sulphur dioxide and sulphuric acid mist. Emissions can be minimized by using the double contact process and fibre mist eliminators. Fluorides are released in the manufacture of phosphoric acid and emissions to the atmosphere are controlled by wet scrubbing. This gives rise to a water pollution problem, however, unless some attempt is made to recover fluorine compounds for sale. Large tonnages of by-product gypsum are produced in phosphoric acid manufacture, which gives rise to a difficult disposal problem. The most satisfactory method is disposal by pipeline to the sea or a tidal estuary. The use of by-product gypsum in the manufacture of building materials is practised on a small scale, particularly in Germany. Losses of ammonia and entrained ammonium nitrate in the steam which is evolved in the manufacture

of ammonium nitrate can be minimized by careful design of the neutralizer and the use of two stages of neutralization. The water rejected in the concentration of urea contains significant quantities of dissolved urea and ammonia, which can be reduced by a hydrolysis and stripping process. There are many variations in processes for the manufacture of compound NPK fertilizers, but all can give rise to losses of ammonia, fertilizer dust and fluorides. Overall losses of valuable raw materials to the environment can be minimized by the use of dry cyclones, wet scrubbing and recirculation of recovered materials to the process. As in phosphoric acid manufacture, control of atmospheric pollution by fluorides gives rise to an aqueous effluent, but the quantities of fluorine involved are relatively small, particularly in nitrophosphate processes. Losses of dust and fume from prilling towers are not easily controlled by scrubbing, but they can be minimized by careful design. Full details of the above and other effluents are given in the relevant sections of this report. A summary table giving estimates of typical effluents and the degree of control available with the best modern technology is provided in the conclusion to the report. Estimates are made of the cost of applying modern pollution control techniques to fertilizer processes, and the effect of legislation on the economics of pollution control is assessed.

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INTRODUCTION

This final report presents the results of studies made during the period January-December 1973 of the pollution problems arising in the manufacture of nitrogenous and phosphate fertilizers. The preliminary report[1], submitted in September 1973, emphasized current technology in the fertilizer industry in the countries of the EEC. The present report includes all the information previously discussed, with some minor corrections and modifications, but a greater emphasis has been laid on the economic aspects of pollution control. In addition coverage is given to a number of topics which were not included in the preliminary report. The most important of these is an estimate of the environmental impact of the various pollutants discharged by the fertilizer industry. This includes a description of the toxic effects of the pollutants and estimates of the total quantities discharged to the environment. Aqueous effluents from a fertilizer factory contain mainly inorganic contaminants so that oxygen demand is not a major pollution factor. Ammonia and urea can, however, exert an oxygen demand and this is discussed. A section at the end of the report pays some attention to a number of general topics, not specific to the fertilizer industry but of importance to it. A summary of legislation applicable to the industry in EEC countries and the USA is included as Appendix A.

The report is divided into sections specific to the individual manufacturing processes which are operated, each comprising a process description, identification of potential sources of pollution, and a discussion of the techniques available for pollution control. A brief summary is included at the end of the longer and more complicated sections. The processes which are given detailed consideration are:

Ammonia
Nitric Acid
Sulphuric Acid
Phosphoric Acid and Superphosphates
Ammonium Nitrate
Ammonium Sulphate
Ammonium Phosphates
Urea
Compound and Complex Fertilizers, including
  Granulation Processes

Sources of Information

There is only a very limited quantity of published information on the effluents from fertilizer manufacture in the EEC countries. There is considerably more information available about the industry in the USA, and there are two comprehensive reports on the manufacture of fertilizer products in Sweden. Information from these sources outside the EEC has been used freely, but as far as possible comparison has been made with information obtained from the literature and chemical plant contractors, in order to assess the validity of the information with respect to European practice. In most cases there is reasonable consistency between data obtained from different sources.

Visits have been made to the major fertilizer manufacturers in the UK, who have all been very cooperative. Contact has also been made with firms in the other EEC countries, mainly through the members of the ISMA/APEA Working Party on Pollution Control in the Fertilizer Industry. A meeting was held with some members of this Working Party to discuss their comments on the preliminary report. The meeting was very valuable and constructive and the expert views of the members of the Working Party have been taken into account in the preparation of this final report.

The Scope and Limitations of the Survey

There are a number of possible reasons why pollution problems arise in the chemical industry. The most important ones in the manufacture of fertilizers are the following:

(1) Limitations to process efficiency under the conditions prevailing in the plant, resulting in the discharge of unreacted raw materials e.g. tail-gases from nitric acid and sulphuric acid plants.

(2) Unwanted by-products due to impurities in raw materials or undesirable side reactions e.g. fluorides and gypsum from phosphoric acid plants, contaminants in process condensate from ammonia plants.

(3) Water rejection as steam in neutralization processes - ammonia can have a significant vapour pressure and be carried off in the steam.

(4) Adventitious losses of raw materials and/or products from processes e.g. dust losses from granulation plants and prilling towers, process leaks and spills.

Discharge of pollutants to the environment from the first three categories is governed by well-defined physico-chemical and engineering principles. It is therefore possible to come to reasonably general conclusions about the amounts of pollutant discharged and the efficiency of techniques used to control them. It is more difficult to come to general conclusions about losses in the fourth category. Some general information is available about dust losses, but much will depend upon the design of each individual plant and the standard of plant maintenance. Process leaks and spills, as well as dissolved fertilizer dust in water used to wash down the plant or storm water may make a considerable contribution to the overall aqueous effluent from a fertilizer factory. Another contribution will come from wet scrubbers used for air pollution control, the extent of which will depend upon the degree of recycling of scrubber liquors. It is impossible to come to any general conclusions on this subject within the scope of the present survey. The composition of the aqueous effluent will vary widely between different plants, and will normally vary from day to day in any individual plant. In many cases effluent streams from different plants (possibly including processes other than fertilizer processes) are combined, and the composition of individual waste streams is not monitored.

It has been emphasized to the author that the methods and costs of pollution control are intimately related to the individual plant. Detailed information on the economics of pollution control is, in general, not available. It has been possible, however, to obtain some approximate estimates of the costs involved in some processes. The figures quoted are only intended as a rough guide and do not refer to any specific plant. Indeed, many of the control techniques described in this report have only recently been developed beyond the pilot plant stage and it is not yet possible to say whether the costs calculated from design parameters can be achieved in full scale operation on a long term basis. Comparison of economic data from different countries is difficult because of the recent fluctuations in exchange rates. It has therefore been decided to quote all costs in the currency of the country where the information originated. To provide some basis for comparison, however, all costs have also been expressed in US dollars, as is normal practice in the literature. The mean exchange rates from January to July 1973 have been used to obtain the following conversion rates:

$1.00	=	Fr	4.4	(France)
		B.Fr	38.2	(Belgium)
		Fl	2.8	(Netherlands)
		DM	2.7	(Germany)
		£	0.4	(UK)

The report also includes estimates made in the USA of the costs involved in meeting effluent standards proposed by the Environmental Protection Agency (EPA). Conversion of all costs into dollars facilitates comparison with these American estimates of the cost of pollution control.

The cost of pollution control techniques depends upon a number of factors e.g. amortization of capital expenditure, the cost of fuel, the cost of steam, and credits for recovered materials. As far as possible the economic data in this report have been put on a common basis by assuming standard values for the cost of steam, raw materials and fuel. The recent large increases in the price of oil will mean that these assumed values will become out-of-date very quickly, and that the cost of pollution control techniques which use large quantities of fuel and heat will increase considerably. Capital charges will vary from site to site and will be very dependent upon the prevailing interest rate when the capital is raised. Although interest rates are very high at present, it seems unlikely that they will increase at as high a rate as prices of fuel and raw materials. Capital charges have been estimated by assuming that the total annual cost of depreciation, interest on capital, maintenance and taxes amounts to 30% of the capital cost of the equipment. Although crude, it is felt that this method is reasonably representative of current West European conditions, and it is compatible with the approximate nature of the generalized economic data presented in this report.

AMMONIA

Process Description

Modern ammonia synthesis technology is based upon the work of Haber and Bosch at the beginning of the century. The basic reaction is

$$N_2 + 3H_2 \longrightarrow 2NH_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

which takes place at high pressure over a catalyst, which was originally osmium, but is now iron promoted with oxides such as CaO, Al_2O_3, MgO, K_2O and SiO_2. The source of nitrogen for the reaction has always been air, but in recent years there have been major changes in the methods of producing hydrogen. Originally obtained by reacting coke and steam in the water gas process or from coke oven gas, the hydrogen in most modern plants is obtained by steam reforming of natural gas, refinery gas or light naphtha. The Texaco and Shell partial oxidation processes, which use liquid hydrocarbon feed stocks, have also gained limited acceptance, but at the present time steam reforming of naphtha or natural gas is the most favoured process.

A simplified flow sheet for a modern ammonia process is shown in Fig. 1. The first step is desulphurization of the feedstock because the reforming catalyst is poisoned by sulphur. Activated carbon or zinc oxide can be used to absorb sulphur compounds from low-sulphur feedstocks. If the organic sulphur content is high catalytic hydro-desulphurization over a cobalt molybdate catalyst can be used, but this requires recycling of part (less than 1%) of the ammonia synthesis gas and is more expensive.

The desulphurized gas is compressed, mixed with steam in excess and passes to the primary reformer. Over the last ten years the reformer pressure has increased from around 10 to around 30 atmospheres* in medium to large plants. The reaction between the hydrocarbon and steam takes place at 800-850°C over a nickel catalyst:

$$Cx\,Hy + xH_2O \rightarrow x\,CO \rightarrow (x + \frac{y}{2})\,H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

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*1 standard atmosphere = 101.325 kN/m^2

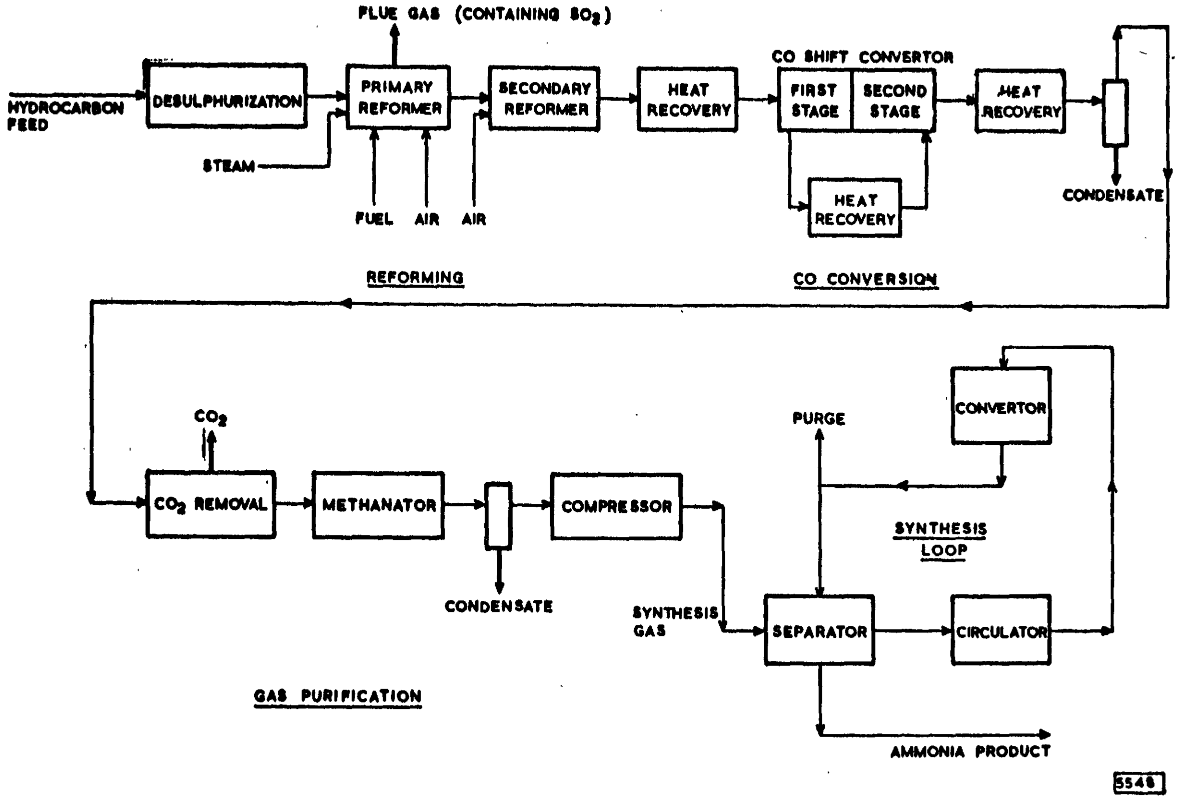


FIG. 1 FLOW SHEET FOR AMMONIA PRODUCTION

The reaction products are mixed with sufficient air to establish the necessary nitrogen stoichiometry and sent to the secondary reformer. Heat liberated by the partial oxidation of the hydrogen and hydrocarbons raises the gas temperature and completes the conversion. The gas mixture is then cooled to about 400°C, mixed with high pressure steam and fed to the shift convertor where the carbon monoxide is converted to carbon dioxide:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The next step is the removal of carbon dioxide. Modern plants scrub the gas with either ethanolamines (usually mono-ethanolamine) or hot aqueous potassium carbonate solutions. A few years ago ethanolamine systems required lower capital expenditure than hot carbonate systems and were preferred, particularly in the USA. Hot carbonate systems, however, require less energy for regeneration and the capital costs have been reduced. They are now widely employed in modern ammonia plants. A number of proprietary systems exist which differ in the additives used to activate the system. The most common are the Vetrocoke system, which uses arsenic trioxide as promoter, and the Benfield system, which incorporates diethanolamine and vanadium pentoxide as a corrosion inhibitor.

Carbon monoxide is an irreversible poison for the synthesis catalyst and must be reduced to a few parts per million in the synthesis gas. One of the oldest processes is to scrub with copper liquor (cuprous ammonium acetate or cuprous ammonium formate) and this method is still used in older plants. A liquid nitrogen wash is very efficient, but is only economical in partial oxidation plants where a liquid air plant is part of the equipment. Most modern plants use catalytic methanation over a supported nickel catalyst.

The purified synthesis gas is then compressed and proceeds to the ammonia synthesis loop, where it mixes with the ammonia-containing gas stream from the convertor. Large plants built in the last ten years (600-1000 tonnes/d) use centrifugal compressors to achieve a synthesis pressure of about 150 atmospheres. Older and smaller plants use reciprocating compressors and a higher synthesis pressure. The gas stream in the synthesis loop is cooled to condense the ammonia present and the product is removed in a gas liquid separator. Conversion is low and so the unreacted gases are recirculated to the convertor. In order to prevent the build-up of inerts in the gas stream a small portion of the gas is continually purged from the system. The synthesis reaction is exothermic and a considerable amount of heat must be removed from the convertor by water cooling. The ammonia from the separator is depressurized in a let-down system and the gases that were in solution are flashed off.

In the partial oxidation process the hydrocarbon feed and oxygen (or oxygen-enriched air) are preheated separately and then reacted at 1400°C and 30 atmospheres to form carbon monoxide and hydrogen:

$$CxHy + \frac{x}{2} O_2 \rightarrow x\ CO + \frac{y}{2} H_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

A further reaction occurs which results in the formation of carbon

$$2CO \rightarrow CO_2 + C \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

The oxygen for the reaction is supplied by a liquid-air plant.

Sources of Pollution

A modern ammonia plant is relatively pollution free. There are two sources of continuous emission to the atmosphere, the flue gas from the primary reformer furnace, and the carbon dioxide released from the process gas stream. There will also be occasional escapes of ammonia from leaks and intermittent escapes from pressure relief valves. There is an aqueous process condensate stream, which may be combined with process leaks and spills to give a single waste stream.

Air Pollution

The sulphur dioxide content of the flue gas will, of course, depend upon the sulphur content of the fuel. For example, if naphtha containing 200 ppm of sulphur is used as fuel approximately 0.2 kg of sulphur dioxide will be emitted per tonne of ammonia produced. If catalytic hydrodesulphurization is used to desulphurize a relatively high sulphur feedstock, the sulphur will be converted to hydrogen sulphide, which will probably be burned in the furnace, adding to the sulphur dioxide emitted in the flue gas. Sulphur dioxide emission is, however, considered to be of minor importance and the only control technique used is dispersion from a high stack.

Carbon dioxide from an ammonia plant is likewise not considered to be a serious air pollutant. The process produces 1.14 tonnes of carbon dioxide per tonne of ammonia when methane is used as feedstock, and there will be additional carbon dioxide in the furnace flue gas. The process carbon dioxide is often used to make urea. Alternatively it can be recovered for sale or discharged to the atmosphere.

The purge gas is too valuable to be allowed to escape to the atmosphere. It is normally scrubbed to recover ammonia which can be sold as aqueous ammonia or distilled to yield liquid ammonia. Hydrogen can also be recovered and the residual gases burned in the reformer furnace. Purge gas can also be used as fuel for a nitric acid plant tail-gas combustion unit.

There will be intermittent emissions of ammonia from pressure relief valves. The atmosphere around a fertilizer factory is usually acidic, particularly if carbon dioxide is allowed to escape. Ammonia emissions can therefore lead to the formation of dense white clouds of ammonium compounds. This problem can be avoided by flaring ammonia emissions from relief valves. It is, of course, necessary to add a fuel gas to the ammonia.

Water Pollution

When the process gas stream from the reformer is cooled the process condensate is formed from the unreacted steam. This waste stream will contain a number of dissolved impurities. Ammonia is formed unintentionally in the first stage of shift conversion in the presence of the iron-containing catalyst and some is dissolved in the process condensate. In addition the condensate is saturated with carbon dioxide, so the ammonia will be in the form of ammonium bicarbonate. There will also be organic matter present, mainly methanol, formed in the second stage of shift conversion, in which a copper catalyst is used. In addition there will be small amounts of sodium, iron, copper, zinc, calcium, magnesium and silica from contact with catalysts, vessel walls and internal refractory materials.

Some data on the composition of the process condensate are given in Table 1. The actual composition in any plant will depend upon the reformer catalyst used. Ammonia concentrations as high as 1000 g/m^3 are more common in the USA than in Europe. In addition to the components quoted in the table, small concentrations (i.e. a few g/m^3) of methylamine have been detected in the condensate from some plants.

TABLE 1. - Ammonia Plant Process Condensate and Waste Water Streams

Quantity m^3/tonne NH_3	Components of Waste Stream, g/m^3							Reference
	Ammonia	Carbon Dioxide	Methanol	Mono-ethanolamine	BOD	COD	Oil	
1.2*	1000	2600	2000-4000	-	-	-	-	2
1.5*	400	700	500	-	-	-	-	3
0.4 - 4.0†	10-100	150-750	-	50-100	50-150	60-200	100-10 000	4

*Process condensate only

†Combined waste stream including leaks and spills

The results of a survey of 16 ammonia plants in the USA are also given in Table 1. These results refer to a combined waste stream comprising the process condensate and water used to wash process leaks and spills, and in-plant clean-up. Apart from the dilution of the process condensate some additional components are present. Mono-ethanolamine comes from the tendency of this carbon dioxide removal agent to be introduced into the gas stream. This component would be rare in European plants, where hot carbonate systems are preferred. Oil comes from the compressors and is introduced into the waste stream with storm water or water used in washing leaks and spills. The survey included some older plants of obsolescent design, and this accounts for the wide ranges of concentrations quoted.

In the partial oxidation of heavy fuel oils the carbon particles produced in the reaction must be scrubbed from the gas stream. An aqueous carbon slurry is produced containing about 3% of the total carbon fed to the primary reaction. This carbon can be processed and returned to the gasification reactor or burned in a boiler[5].

When copper liquor is used for carbon monoxide removal, there may be a contribution to the aqueous effluent from leaks and spills. No information has been made available concerning the quantities involved.

Miscellaneous Wastes

Hot carbonate carbon dioxide removal processes are completely self-contained recirculating systems and the materials used do not normally get into effluent streams. In case of leaks it is important that precautions should be taken to avoid contamination of waste water, particularly when arsenic is present. If there is an accidental arsenic spillage, lime and ferrous sulphate can be used to precipitate calcium iron arsenate. There have been occasional accidents when a fracture in the equipment has led to large quantities of arsenic being discharged into the atmosphere. Such incidents are fortunately very rare but when they do occur they can be very dangerous. When carbon dioxide is vented to the atmosphere it should be pre-cooled to remove condensate and this provides some control in case of accidents. Escape from the Benfield system is regarded as less dangerous, but vanadium pentoxide powder is hazardous to plant operators when handled.

An arsenical sludge can build up in the Vetrocoke system and this must be disposed of from time to time. Deep-sea dumping is the safest way of disposing of this material. Other occasional solid waste disposal problems include spent catalyst and saturated zinc oxide used for desulphurization.

Control Techniques

Apart from dispersion of gases by a chimney and dilution of process condensate with other waste streams before discharge very little is done to control the effluents from most ammonia plants. Process condensate has been used as cooling tower make-up in some older ammonia plants, where a lower reformer pressure resulted in lower concentrations of ammonia and organics in the condensate. This is not regarded as advisable in modern plants[6]. The condensate can, however, be steam stripped to remove most of the ammonia and most of the organic material, and a process has been developed which allows the stripped condensate to be used as boiler feed water[2,6]. The process is new and can not yet be considered proven for consistent full scale operation.

The condensate is fed to a stripping tower to remove the volatile gases (ammonia, carbon dioxide and methanol). Ammonia can be recovered as an aqueous solution. The stripped condensate is expected to have concentrations of ammonia, carbon dioxide and methanol of about 20, 40 and 50 mg/l respectively. Heavy metals are then removed and replaced by ammonium ions in an ion exchange unit, which produces boiler feed water of comparable quality to demineralized water with respect to heavy metals. Condensate produced downstream of the carbon dioxide removal unit may be contaminated with potassium carbonate solution and cannot be used in this way[7].

The process recycles the process condensate and eliminates this stream with its ammonia content as a plant effluent. It also reduces the demand for demineralized boiler feed water and therefore reduces the effluent produced in regeneration of the ion exchange resins. The overall plant effluent is stated to be reduced by 30 per cent. About three units have been constructed in the USA and one in Holland.

A simple stripping tower on a 900 tonne/d ammonia plant vented to the atmosphere could cost about $150 000. This would merely substitute an air pollution problem for a water pollution problem, however, and a reflux column for recovery and concentration of the ammonia solution would cost twice as much. The most important contribution to the running costs come from capital charges and the cost of steam at a pressure of 3.3 kg/cm^2. Steam requirements have been quoted as 1.2 lb/US gall for a stripping tower vented to the atmosphere, and 2.0 lb/US gall for a reflux column. For a 900 tonne/d plant these figures correspond to 0.17 and 0.29 tonnes of steam per tonne of ammonia respectively. The running costs are summarized in Table 2.

The value of the ammonia recovered in a reflux column is quite small and does not compensate for the extra cost of the equipment. The higher price must be paid, however, if it is desired to reduce both water and air pollution from the plant to the maximum possible extent. The cost will be even higher if an ion exchange unit is included.

Summary

Air pollution from ammonia plants is of minor importance. Small quantities of sulphur dioxide may be emitted from the primary reformer furnace and carbon dioxide will be released to the atmosphere if it is not used for urea manufacture or recovered for sale. There will be intermittent emissions of ammonia from relief valves. The major

TABLE 2. - Running Costs for Steam Stripping of 900 tonne/d Ammonia Plant Condensate

Type of Column	Vented to Atmosphere	Reflux
Costs in $/tonne NH_3		
Capital Charges (at 30% per annum)	0.15	0.30
Steam (at $1.90/tonne)	0.32	0.55
Credit for NH_3 Recovery (assuming 1000 g/m^3 in condensate and a value of $50/tonne		-0.06
Net Cost of Treatment	0.47	0.79

problem is water pollution from the process condensate. A stripping process has been developed which can recover ammonia from the condensate and produce water of sufficiently high purity for use as boiler feed water. The cost of treatment for a 900 tonne/d plant is $0.47/tonne of product if the stripped ammonia is vented to the atmosphere, and $0.79/tonne of product if it is recovered in a reflux column. At the present time it is probable that most ammonia plants discharge the condensate to drain.

NITRIC ACID

Process Description

At the present time all commercial processes for the manufacture of nitric acid are based upon the catalytic oxidation of ammonia. There are several different proprietary processes available. Although they all use the same basic route to produce nitric acid at concentrations between 50 and 70 per cent, they employ different operating conditions, depending to a large extent upon the effect of local conditions on the economics of production. Basically a modern nitric acid process proceeds in two stages:

(i) Ammonia is oxidized with air in a catalytic converter containing a pad of platinum-rhodium gauzes. A rapid exothermic reaction takes place at 800-960°C and nitric oxide is produced.

$$4NH_3 + 5\,O_2 \rightarrow 4NO + 6H_2O + 216.6\ \text{k.cal} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The heat of reaction is recovered in waste heat boilers. Gases leaving the boilers are cooled and most of the water is condensed out. The condensate, a dilute solution of nitric acid, is used in the absorption tower.

(ii) The gases pass into the absorption tower together with air and water. The nitric oxide reacts with oxygen homogeneously in the gas phase to form nitrogen dioxide, which is then absorbed in water.

$$2NO + O_2 \rightarrow 2NO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The nitric oxide produced by Reaction (3) in the liquid phase is reoxidized to nitrogen dioxide in the spaces between the trays in the absorption column.

Ammonia conversion to nitric oxide is favoured by low pressures whereas the reactions in the absorption tower are assisted by elevated pressures and low temperatures. Early nitric acid plants operated at near atmospheric pressure and required immense absorption systems. The development of corrosion resistant stainless steels made it possible to carry out absorption under pressure and this led to the typical European mixed-pressure process in which the nitrous gases formed by ammonia oxidation at low pressure are compressed before being absorbed in a stainless steel column. In the United States the emphasis has been on high mono-pressure plants in which capital savings due to reduction in the volume of the plant and the elimination of expensive nitrous gas compressors offset lower efficiency and higher catalyst losses in the ammonia convertor (Table 3). In recent years lower ammonia prices and increasing interest rates have led to a tendency towards the latter type of process in Europe, and a number of mono-pressure plants operating at medium (<6.5 atmospheres) or high pressure

TABLE 3. - Effect of Pressure on Ammonia Converter

	Pressure		
	atmospheric	medium	high
Gauze Temperature (°C)	800	845-880	900
Efficiency	98%	-	92%
Catalyst Losses (mg/tonne 100% HNO_3)	50	85-125	250-400
Gauze Change	Up to 6 months	3 months	4-8 weeks

(>6.5 atmospheres) have been built. A mixed-pressure plant can still be an economical choice where the price of ammonia is relatively high, and recently built plants (mainly in Eastern Europe) carry out ammonia oxidation at 3-4 atmospheres and absorption at 10-13 atmospheres. Such plants tend to be very large (around 1000 tonne/d capacity) and involve high capital investment.

Sources of Pollution

The only continuous source of pollution from a nitric acid plant is the tail-gas from the absorption tower which contains oxides of nitrogen. This is illustrated in the simplified flow sheet for a typical mono-pressure process in Fig. 2. There will be an intermittent aqueous effluent from leaks, the extent of which will be dependent upon plant operation and maintenance.

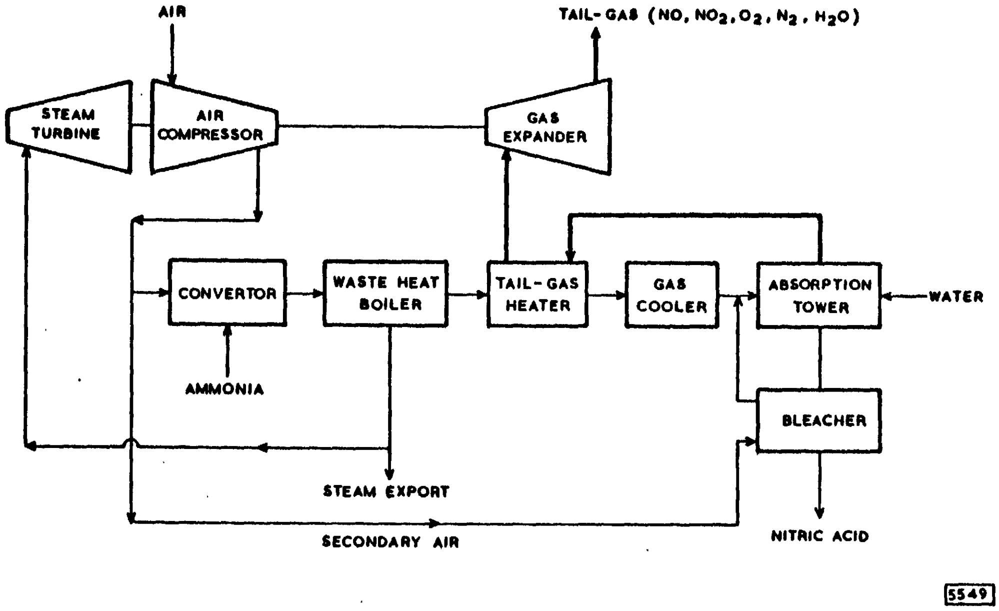


FIG. 2 FLOW SHEET FOR A TYPICAL MONO-PRESSURE NITRIC ACID PROCESS

The composition of the tail-gas depends upon the efficiency of the absorption system. Older atmospheric pressure plants frequently used an alkaline absorption tower following the water absorption towers to reduce the nitrogen oxides to the 3000 ppm level. A plant of this type was built by ICI in 1949 to operate at 1.2 atmospheres absolute[8]. A more recent ICI plant[9] illustrates the trend to higher absorption pressures. A mixed-pressure plant was chosen in which absorption was carried out at 4 atmospheres absolute, and this enabled a concentration of less than 3000 ppm of nitrogen oxides in the tail-gas to be achieved without further treatment. All modern processes carry out absorption at not less than 3 atmospheres, achieving absorption efficiencies of between 98.2 and 99.3 per cent[10]. Typical tail-gas composition would be:

NO, NO_2 (NO_x) : 800-3000 ppm by volume
Oxygen : 2-3.5% by volume
Water : 1%
Nitrogen : Balance

In hot weather the nitrogen oxide concentration can be even higher, possibly as high as 5000 ppm. At 1000 ppm the emission of nitrogen oxides, calculated as NO_2, amounts to about 7 kg per tonne of 100% nitric acid produced. A major part of the effluent is in the form of nitrogen dioxide and this gives rise to the typical red-brown colour of the plume from a nitric acid plant stack.

Published measurements of emissions from plants are scarce. Tests at 12 plants in the United States, not equipped with control equipment, showed an emission range of 1000-6900 ppm of nitrogen oxides, with an average value of 3700 ppm[11]. Nitrogen dioxide accounted for between a third and a half of these values. Concentrations of 2800 ppm and 4000 ppm in undiluted tail-gas were observed at two plants in Sweden[12]; lower values of 300 ppm and 800 ppm were obtained on another two plants where the tail-gas was diluted with air. Of greater interest for the present study are the results of observations made at 5 nitric acid plants in Germany[13], where the concentration of nitrogen oxides emitted was in the range 2000-3000 ppm. Measurements of ground level concentrations near these plants are described in the section on the environmental impact of pollution.

Control Techniques

A large body of technology has been developed for treating tail-gas from nitric acid plants and a number of general reviews of the subject have been published[14-16]. The techniques used fall into six classes:

Wet Scrubbing
Incineration
Dilution and Dispersion
Increased Absorption Capacity
Catalytic Reduction
Adsorption

Wet Scrubbing

Alkali scrubbing is still used as a method of controlling the effluent, particularly in older low pressure nitric acid plants. It has been shown to be capable of removing at least 90% of the nitrogen oxides in the tail-gas[17] and concentrations as low as 100 ppm have been achieved[18]. In the latter case the method was used for purification of gases from nitration processes combined with a small nitric acid plant and the results cannot be considered as typical. The present state of the art in alkali scrubbing is illustrated by a plant being built in Italy, for which 600 ppm is guaranteed. The method has the great disadvantage of producing a liquid by-product for which a use or method of disposal must be found. It appears that the method is usually employed when the company concerned is a general chemical producer with a use or market for the sodium nitrite/nitrate produced. Other scrubbing systems have received attention[16] but none of these has achieved commercial application.

Incineration

Incineration in a flare can be used to reduce nitrogen dioxide to nitric oxide producing a colourless effluent. It is usually regarded as too costly in fuel for satisfactory application to nitric acid tail-gas. The method has been used in the United States to treat an effluent stream containing more than 10 per cent of nitrogen oxides[19].

Dilution and Dispersion

The policy of dilution of the tail-gas by mixing with additional air or steam is widely employed in Europe, usually in conjunction with dispersion of the gases by means of a high stack. The aim is to lower the ground level concentration of the nitrogen oxides in the vicinity of the plant to a level which is considered to be safe, although the total quantity of pollutant discharged is not reduced. The UK Alkali Inspectorate permits a maximum three minutes ground level concentration of 0.16 ppm expressed as NO_2 and has published a table of recommended stack heights based upon an undiluted discharge of 2700 ppm of NO_2[20].

TABLE 4. - Recommended Stack Heights for Nitric Acid Plants

Tonnes of 100% HNO_3 per day	Recommended Stack Height
175	180 ft (55 m)
350	250 ft (76.5 m)
530	300 ft (91.5 m)
700	350 ft (107 m)
1050	400 ft (122 m)

The methods adopted for the calculation of stack heights vary from country to country. The figures in Table 4 are reproduced to give an example of the order of magnitude of typical nitric acid plant stacks. Modern plants are designed to give nitrogen oxide emissions at considerably lower concentrations than 2700 ppm but UK manufacturers are still urged to provide high stacks as a safety measure for occasions when the plant is not operated at optimum efficiency. The stack makes a significant contribution (4-8%) to the capital cost of the plant.

Increased Absorption Capacity

The most obvious way of reducing nitrogen oxide emissions is by providing increased capacity in the absorption tower. The oxidation of nitric oxide is a relatively slow reaction, however, and becomes the rate controlling step as the concentration remaining in the tail-gas is reduced. It therefore requires increasingly larger equipment to accomplish further reduction in concentration, and the cost for improved absorption rises exponentially as lower levels of nitrogen oxides are sought. Opinions differ somewhat on the degree of control that can be achieved. According to Newman[21], calculations for a mono-pressure plant operating at 9 atmospheres show that increased product recovery justifies holding nitrogen oxide emissions in the range of 1500-2000 ppm for economic reasons alone. Figure 3 shows how the most economical and minimum emission levels vary with pressure in the absorber. Oxide emission can be reduced to below 300 ppm, but very high pressures are required and the cost is high. The most economical emission level in Fig. 3 will depend upon the price of ammonia. The curves in the figures were calculated using an American high pressure plant as a reference and the values quoted are only approximate. The overall shapes of graphs can be assumed, however to have general validity.

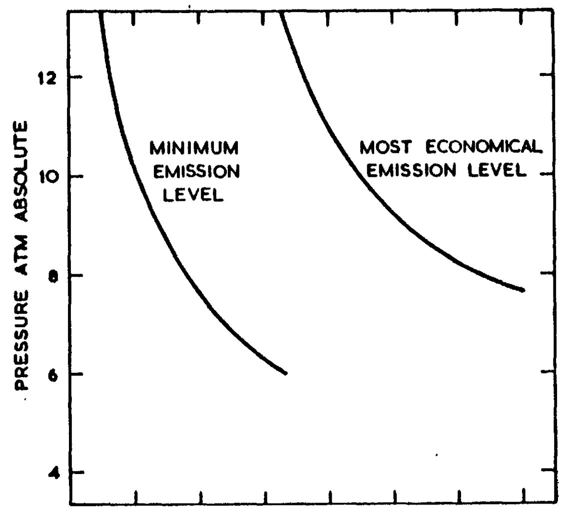


FIG. 3 VARIATION OF NO_x EMISSIONS WITH ABSORPTION PRESSURE

As shown in Fig. 3 the pressure required in the absorption tower increases exponentially as the nitrogen oxide concentration is reduced. As a general guide, for a given nitrogen oxide concentration, the volume of the absorption tower varies inversely as the square of the pressure.

Mayland and Heinze[22] have proposed a process in which the nitrogen oxides are absorbed in dilute nitric acid in a column with a catalytic packing to recover them as nitric acid. It is claimed that the nitrogen oxide concentration in the tail-gas can be reduced from 3000 ppm to 200 ppm, and at the same time the production of nitric acid is increased by 3 per cent.

Conditions for achieving low emission levels should be very favourable in mixed-pressure processes because it is possible to achieve very high absorption pressures while keeping the ammonia conversion efficiency and catalyst losses within acceptable limits. Nitrous gas compression equipment is very expensive but the cost varies considerably with plant size. Higher operating pressures also mean that the volume of the absorption system can be decreased, and mixed-pressure systems with absorption pressures of 10-13 atmospheres become economical for very large plants (greater than ca.700 tonne/d). The economical nitrogen oxide concentration in the tail-gas tends to be low in these plants. A lower limit of 200-300 ppm is probably achievable by high pressure adsorption, but 600 ppm is probably a reasonable average for high pressure plants with extended absorption capacity.

Catalytic Reduction

The use of catalytic combustion on nitric acid plants originated as a system for improved heat recovery. A fuel gas was added to the tail-gas and passed over a catalyst to react with the oxygen in the tail-gas. In this way the gas mixture was heated to 670°C so that most of the power required for compression could be recovered in a high temperature turbo-expander[21]. It was found that the nitrogen dioxide reacted simultaneously with the fuel to yield nitric oxide, thus causing decolourization of the effluent gas. It has been reported that approximately one-third of the nitric acid plants in the United States have been fitted with decolourization and power recovery equipment[23]. While producing no real pollution abatement, it does make the effluent invisible and removes a major source of complaints from the public. Of course, nitric oxide will be re-oxidized in the atmosphere, but dispersion of the gases is usually sufficiently rapid for the re-appearance of colour not to be apparent.

Suitable fuels are hydrogen (e.g. ammonia synthesis-loop purge gas), naphtha and natural gas (methane), the choice depending upon availability and price. The reactions which occur with methane are as follows:

$$CH_4 + 4NO_2 \rightarrow 4NO + CO_2 + 2H_2O \quad \ldots\ldots\ldots\ldots (4)$$

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2H_2O \quad \ldots\ldots\ldots\ldots (5)$$

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \quad \ldots\ldots\ldots\ldots (6)$$

Similar equations can be written substituting hydrogen for methane. The decolourization Reaction (4) is faster than Reaction (5), and decolourization can therefore be achieved in the presence of oxygen. The abatement Reaction (6), on the other hand, is much slower than Reaction (5). In order to reduce the nitrogen oxides to nitrogen sufficient fuel must be added to react with all the oxygen in the tail-gas and in practice an excess of fuel is used. The temperature rise which occurs is proportional to the oxygen content of the tail-gas and, as a general rule, the following values can be assumed for each one per cent of oxygen that is burned:

Hydrogen : 160°C
Hydrocarbons : 130°C

Minimum inlet temperatures for ignition are:

Hydrogen : 200°C
Naphtha : 350°C
Natural Gas : 480°C

The temperature limit for the catalyst is 750-850°C and this sets a limit on the amount of oxygen that can be removed in a single stage. For example, when methane is used as fuel with an inlet temperature of 480°C the maximum oxygen concentration lies in the range 2-3 per cent. It is necessary to cool the exhaust gases in a waste heat boiler in order to meet the temperature limit of the turbo-expander. Two stage systems have been designed in which most of the oxygen is removed in the first stage and the second stage is run under reducing conditions for abatement. Both palladium and platinum have been used as catalysts, supported on either pelleted or honeycomb ceramic supports. There has been much discussion about the relative merits of the various catalyst systems[14,24-26].

In practical operation catalytic tail-gas reduction has acquired a poor reputation. Many units have achieved abatement for only a few weeks, after which declining catalyst activity has resulted in increasing nitric oxide levels. Reasons for reduced activity include catalyst poisoning, thermal degradation and carbon deposition[23]. Excessive temperatures in the reactor have been known to be sufficient to cause melting of the ceramic support. The general feeling among nitric acid manufacturers is that although catalytic decolourization is a proven technique, consistent abatement over a long period of time has still to be demonstrated. There is, however, a recent report which indicates that the problems of operating catalytic reduction may have been solved[27]. The BASF Antwerpen plant has been operating with an average concentration of 100-200 ppm in the tail-gas for well over a year. A small problem which has been experienced is poisoning of the catalyst by chromium leached from stainless steel by nitric acid mist. This has made it necessary to change the first stage catalyst after 17 months. If this problem could be avoided the catalyst should last for 2-3 years. The catalytic combustor is a two-stage unit using a honeycomb supported platinum catalyst and natural gas as fuel. Successful operation of a catalytic abatement unit in the UK is also reported, using ammonia purge gas as fuel.

Even when operated successfully catalytic tail-gas reduction does not completely eliminate air pollution from the plant. Although low nitrogen oxide concentrations can be achieved, the tail-gas will contain unburned fuel. When the fuel is a hydrocarbon carbon monoxide can be expected as a product of combustion. In emission tests on catalyst beds operated to achieve nitrogen oxide concentrations of 200 and 46 ppm, carbon monoxide concentrations of 600 and 3000 ppm respectively were observed[28]. It was also calculated that, under the same conditions, hydrogen cyanide may be generated in concentrations of 200 and 600 ppm respectively. The presence of up to 1000 ppm of ammonia has also been reported[29]. No data are available on the concentrations of these gases in the tail-gas from a full scale plant, but the possibility of their presence casts doubt upon the value of tail-gas reduction as a pollution abatement technique.

Selective catalytic abatement using ammonia as fuel has also been proposed, in which nitrogen oxides are reduced to nitrogen without any simultaneous reaction with oxygen:

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \quad \text{(17)}$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \quad \text{(8)}$$

Commercial experience has not so far been satisfactory. A unit on a nitric acid plant in Holland was taken out of service after only 8 weeks when it was discovered that ammonium nitrate and nitrite were being formed downstream. The explosion hazard due to the formation of ammonium nitrite makes further exploitation of this method unlikely.

Adsorption

Adsorption of nitrogen oxides on a solid support followed by regeneration and total recycle to the absorption tower of the nitric acid plant is a potentially attractive method of pollution control. The use of silica gel[30,31] and molecular sieves[31,32] has been studied on a laboratory scale. Molecular sieves have been shown to be the more effective adsorbents[31]. In the United States the Union Carbide Corporation have developed a Molecular Sieve Process[33]. It is claimed that this process can reduce the nitrogen oxide concentration in the tail-gas to less than 10 ppm, and that by recycling a 2.5 per cent yield increase can be obtained. Continuous operation is achieved by using two molecular sieve beds; one bed is regenerated at about 300°C while the other is adsorbing. It remains to be seen how well the process will operate on a long term basis on a commercial nitric acid plant. A unit is under construction in the United States for a 55 tonne/d plant and results of trials on this plant will be of great interest to the industry.

Comparative Economics of Abatement Processes

Of the control techniques which have been described, detailed costs are available for extended absorption capacity, catalytic reduction and molecular sieve adsorption. Comparisons between the economics of operation of different control techniques can only be made in terms of model plants and do not necessarily apply to any existing plant. The choice between these techniques will depend upon local circumstances. Factors such as the availability of space for extra equipment, the cost of fuel, the value of steam and the basic design of the nitric acid process as a whole are all important.

The biggest contribution to additional running costs for extra absorption capacity will come from maintenance and capital charges which can be assumed to be between 20 and 30% per annum of the capital cost of the equipment. There will be an additional cost for cooling and process water, but this is not easily dissociable from the total running cost of the plant. These increased costs are offset to some extent by the value of the increased nitric acid yield in the absorption tower. For a typical high pressure plant of 540 tonne/d nominal capacity and a tail-gas flow rate of 80,000 m^3/h, reducing the nitrogen dioxide concentration from 1500 ppm would increase the yield of nitric acid by 0.7% at 800 ppm and by 1.3% at 200 ppm. Reducing the concentration from 2500 ppm to 200 ppm would increase the yield by about 2%.

There is considerable variation in the estimates made by different contractors for the provision of increased absorption capacity in a new plant. Some data supplied by UK firms are presented in Table 5. These data are based upon a standard 500 tonne/d, 7 atmosphere mono-pressure plant designed for a nitrogen oxide concentration of 1500-1600 ppm in the tail-gas. The cost of the absorption tower in this plant would be in the range £150 000-£200 000 or around 15% of the cost of the plant. The additional cost of a second absorption tower to achieve 800 ppm would probably be slightly less, but of the same order of magnitude. To achieve 800 ppm in a 7 atmosphere plant would therefore involve an additional expenditure of 10-15% of the capital cost of the plant. The same level of control in a 5 atmosphere plant would be considerably more expensive; over 20% of the cost of the plant.

TABLE 5. - Pollution Abatement by Increased Absorption Capacity

Type of Plant*	Economic NO_x conc. (ppm)	Extra Absorption Capacity for 800 ppm	Estimated Cost for 800 ppm from 500 tonne/d plant
7:7	1500-1600	approximately double volume	£150 000 - £180 000 ($375 000 - $450 000)
5:5	2500	approximately twice the volume required for 7:7 plant	£300 000 - £400 000 ($750 000 - $900 000)
4:10	200-800	-	-

*4:10 denotes a plant in which ammonia oxidation is carried out at 4 atmospheres absolute and absorption at 10 atmospheres absolute.

The minimum concentration of oxides of nitrogen achieved in the tail-gas from mono-pressure plants which have been built or are under construction at the present time probably lies in the range 600-800 ppm. If lower levels are sought by provision of extended absorption capacity, most experts would probably recommend a mixed pressure process. The addition of an extra absorption column operating at 6 atmospheres absolute to a 300 tonne/d plant to reduce emissions from 2500 ppm to 200 ppm would cost 2 200 000 francs or $500 000 according to a French contractor[29]. A manufacturer has estimated that the increased cost in a 550 tonne/d plant would be about $1 million. A German contractor, however, claims an equally high degree of pollution control by increased absorption capacity in mono-pressure plants at considerably lower cost, and has supplied the information in Table 6.

TABLE 6. - Pollution Abatement by Increased Absorption Capacity; German Contractors Data

Type of Plant	NO_x in tail-gas, ppm	Increased N yield for NO_x < 1500 ppm	Additional Investment for 600 tonne/d plant	Increased Compressor Power Requirements, kW
Medium Pressure (4.5 atm)	400	0.94%	DM 600 000 ($220 000)	500
High pressure (9 atm)	200	1.08%	DM 650 000 ($240 000)	600

The increased cost is less than 10% of the total cost of the equipment.

The information in the previous paragraphs can be used to derive the approximate increased cost of a tonne of nitric acid which can be attributed to pollution control. The results are summarized in Table 7.

It has unfortunately not been possible to obtain costs for a range of plant sizes and tail-gas compositions from a single source. The figures in Table 7 are from a variety of different sources and they do not permit any conclusions about the effect of the capacity of the plant on the cost of control. The data in the first three columns of the table appear to be consistent with quotations made to manufacturers in the UK. They lead to the conclusion that a nitrogen oxide concentration of 800 ppm in the tail-gas can be achieved at a cost of $0.51-$0.65 per tonne of product, and the cost is approximately doubled if 200 ppm is required. There appears to be very little reduction in the control cost with increasing plant capacity in the range 300-550 tonnes/d. The cost of the German process appears to be considerably lower, but the relative accuracy of these estimates could only be judged by an expert on the basis of design data for individual plants.

The cost of pollution control in very large plants may be quite small. Mixed-pressure plants, with absorption pressures in the range 10-13 atmospheres tend to become the economical choice in the capacity range 700-1000 tonnes/d. A high degree of pollution control is inherent in such plants without additional equipment, and nitrogen oxide concentrations in the range 400-600 ppm (and possibly lower) would be achievable

TABLE 7. - Cost of Pollution Abatement by Increased Absorption Capacity

Type of Plant	300 tonne/d mixed-pressure 200 ppm	550 tonne/d mixed-pressure 200 ppm	500 tonne/d mono-pressure (7 atm) 800 ppm	600 tonne/d mono-pressure (9 atm) 200 ppm
Additional Investment	$500 000	$ 1 million	$375 000 - $450 000	$240 000
Costs in $/tonne HNO_3				
Capital Charges, etc. at 30% per annum	1.52	1.65	0.68-0.82	0.36
Increased Power Requirement at $0.01/kWh	-	-	-	0.24
Credit for Increased Efficiency at $24/tonne HNO_3	-0.48*	-0.48*	-0.17†	-0.25ϕ
Net Increase in Cost of Production	1.04	1.17	0.51-0.65	0.35

*increased efficiency 2%

†increased efficiency 0.7%

ϕincreased efficiency 1.08% (contractors value) at little extra cost. With considerable increases in the prices of naphtha and natural gas likely to occur in the near future, high ammonia conversion efficiencies will become more desirable. There will therefore be a tendency for mixed-pressure plants to become economical at lower capacities.

It is difficult to quote costs for a catalytic tail-gas reduction unit because they depend very much on the design of the nitric acid plant. European plants have tended to use low temperature turbo-expanders for energy recovery and on such a plant it will be necessary to provide heat exchange facilities to heat the tail-gas and fuel mixture to its ignition temperature before passing into the reduction unit. In addition a waste heat boiler will be needed to cool the exhaust gases before they go to the expander. The situation may be quite different if a new plant is being designed. It might be decided to use a high temperature turbo-expander, such as is common in high pressure plants of the type developed in the USA. This choice would be particularly attractive if the value of steam on the site is low. It is not easy to dissociate the cost of the tail-gas reduction unit from the cost of this type of energy recovery system because they are so closely integrated. Indeed, many plants in the USA use catalytic reduction primarily as an energy recovery system, and decolourization (but not abatement) is achieved as a happy side-effect to which no extra cost is ascribed.

The addition of a catalytic reduction unit to an existing plant would be difficult and would probably involve extensive re-design of the plant. There would be a reduction in capacity because of the increased pressure drop through the plant and the need to run at a lower oxygen concentration in the absorption tower.

As a rough guide the following capital costs might apply to the addition of catalytic abatement equipment including a waste heat boiler, to medium pressure plants in the UK fitted with a low temperature turbo-expander.

TABLE 8. - Capital Costs for Catalytic Tail-Gas Reduction

Plant Capacity, tonne /d	Approximate Capital Cost	Approximate Cost of Tail-Gas Reduction Unit
200	£0.75 x 10^6	£100 000 ($250 000)
500	£1.4 x 10^6	£150 000-£170 000 ($375 000-$425 000)

The cost of the additional equipment lies between 10 and 13% of the cost of the plant and is relatively smaller as the capacity increases up to 500-600 tonnes/d. Larger plants would probably be twin-stream, or of the mixed pressure type to which catalytic reduction would be superfluous at the present time.

In addition to the difficulty in deciding what proportion of the capital cost of a catalytic reduction system should be charged to pollution control, it is difficult to make a generally applicable statement about the fuel requirements. Much will depend upon the design of the system and the oxygen content of the tail-gas, and fuel requirements ranging from 0.3 to 1.5 x 10^6 kcal/tonne of nitric acid have been quoted. Some attempts to estimate running costs in various situations, based upon information from several sources, are presented in Table 9. The effects of the reduced pressure drop across the absorption system and changes in tail-gas flow rate are neglected.

The first column in the table refers to a new plant fitted with a high temperature turbo-expander, and having an oxygen content of 2% in the tail-gas. The capital investment of $60 000 for the abatement system does not include any contribution to the cost of the energy recovery system. This system can be very economical to run if the value of steam on the site is high. The quoted value of $1.90/tonne is considered to be a reasonable average. No information is available for a smaller plant of this type, but since capital charges are a relatively small proportion of the running costs, the net cost for a smaller plant would not be very much higher. These costs are based upon data for an operational plant and are considered to be realistic.

The costs for plants B and C refer to new plants fitted with a low temperature turbo-expander and are based on published information[29]. They also represent the minimum costs applicable to adding catalytic reduction to existing plants. They include the cost of adding a waste heat boiler to recover steam for use in the plant, and for export. The quantity of steam generated in this plant will be greater than would be the case in a plant fitted with a high temperature turbo-expander. In plants B and C capital charges make a considerable contribution to the net cost of abatement, which is much higher than the net cost in plant A. The cost is somewhat lower in a 500/tonne/d plant because of a lower contribution from the capital charges.

It is much cheaper to operate a catalytic reduction system which has been included in the design of a new plant than to operate a system which has been added to an older plant. In fact it has been calculated that it is cheaper to manufacture nitric acid in a plant built in 1972 with a catalytic reduction system included, than to manufacture nitric acid in a 1962 plant without tail-gas control.[34] In any case, there is little incentive to modify an existing plant because legislation is seldom retroactive.

The most recent cost data available for molecular sieve adsorption are given in Table 10[35]. Information is only available for a 300 tonne/d plant, for which the total capital investment is $580 000. The net treatment cost is higher than the cost of extended absorption capacity or catalytic reduction, but the nitrogen oxide concentration in the tail-gas should be reduced to less than 50 ppm, and the method would not give rise to other pollutants in the tail-gas. It should be noted that the high cost of molecular sieve adsorption is due to its high capital cost. Running costs would not be greatly affected by increases in the price of fuel and do not depend upon the value of steam.

TABLE 9. - Running Costs for Catalytic Tail-Gas Reduction

Cost in $/tonne of 100% HNO_3

	Plant A, with high temperature turbo-expander	Plants B and C with low temperature turbo-expanders	
	500 tonne/d	300 tonne/d	500 tonne/d
Equipment (at 30% per annum)	0.11	0.83	0.54
Catalyst (2 year life)	0.37	0.37	0.37
Fuel (at $3.00/$10^6$ kcal)	1.08	1.74	1.74
Steam Export (at $1.90/tonne)	-1.43	-1.71	-1.71
Net Cost	0.13	1.23	0.94

Assumptions:

2 stage system using natural gas as fuel and platinum catalyst

Equipment cost includes a waste heat recovery boiler on plants fitted with low temperature turbo-expanders, but no contribution to energy recovery equipment is assumed in the plant with a high temperature turbo-expander

Fuel consumption 0.36×10^6 k cal/tonne HNO_3 in plant A
                     0.58×10^6 k cal/tonne HNO_3 in plants B and C

Steam export   0.75 tonne/tonne HNO_3 in plant A
                 0.90 tonne/tonne HNO_3 in plants B and C

TABLE 10. - Running Costs for Molecular Sieve Adsorption

	Cost of $/tonne of 100% HNO_3
Equipment (at 30% per annum)	1.76
Power (at $0.01/kWh)	0.27
Heat (at $3.00/$10^6$ kcal)	0.12
Cooling Water (at $0.01/$m^3$)	0.13
Molecular Sieve (4 year life	0.15
Credit for HNO_3 recovered (at $24.00/tonne)	-0.69
Net Cost	1.74

Summary

The major problem is air pollution by oxides of nitrogen present in the tail-gas Several techniques are available for pollution abatement, but the most effective at the present time are caustic scrubbing, increased absorption capacity, and catalytic reduction. Adsorption on molecular sieves shows promise, but has not yet been established on a commercial-scale plant. The conclusions made about these control techniques are summarized in Table 11.

SULPHURIC ACID

Process Descriptions

Most sulphuric acid production is by the contact process, and the trend is towards an increasing production in high capacity plants. The older chamber process is gradually declining in importance but it is estimated[36] that there are still between 20 and 30 plants operating in the EEC. Brief consideration will therefore be given to the chamber process but the contact process will be treated in greater detail.

TABLE 11. - Summary of Control Techniques for Air Pollution Control on a Nitric Acid Plant

Control Technique	NO_x Concentration achievable in Tail-gas	Remarks
Caustic Scrubbing	600 ppm	Effective, but introduces by-product disposal problem
Catalytic Reduction	<200 ppm	Effective for decolourization. Long term abatement only recently demonstrated, many plants have failed after a short period of operation. Tail-gas may still contain unburned fuel, CO, NH_3, HCN Estimated capital cost: 10-13% of cost of plant Running costs: $0.13/tonne HNO_3 in a new 500 tonne/d plant with high temperature turbo-expander, $0.94-$1.23 in plants with low temperature turbo-expander
Increased Absorption Capacity	<500 ppm	Recovers nitrogen oxides in product. Plants can be designed for low NO_x concentrations, particularly when absorption pressure is high. Mixed-pressure plants are probably the most economical way of achieving a low NO_x concentration for capacities higher than 700-1000 tonnes/day. Estimates of capital cost vary from 10 to 25% of cost of plant for reduction of NO_x concentration from 1500 ppm to somewhere in the range from 200 to 500 ppm. Running costs: $0.51-$0.65/tonne HNO_3 to achieve 800 ppm in 500/tonne/d plant. $0.35/tonne HNO_3 to achieve 200 ppm claimed in one 9:9 plant, other processes $1.04-$1.17.
Absorption on Molecular Sieve	<50 ppm	Very promising. Not yet proven on commercial scale Estimated Capital Cost: $580,000 for adding a unit to a 300 tonnes/d plant Running costs: $1.74/tonne HNO_3

A simplified flow diagram for the chamber process is shown in Fig. 4. Sulphur dioxide is oxidized in the Glover tower and lead chambers to sulphur trioxide in the presence of nitrogen oxides. The nitrogen oxides are recovered in the Gay Lussac towers by absorption in 78% sulphuric acid. The nitrous vitriol so formed passes to the Glover tower where the nitrogen oxides are released for re-use. The acid made in the chambers (60-70%) is concentrated to 78% in the Glover tower by flowing counter-currently to the hot sulphur dioxide gas. The 78% acid is cooled, part is recycled to the Gay Lussac towers, and the rest is stored as product.

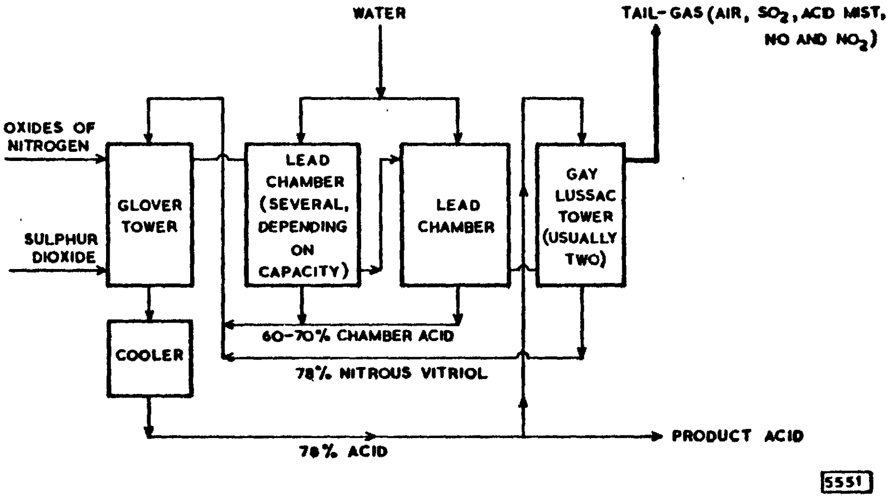


FIG. 4 FLOW SHEET FOR SULPHURIC ACID PRODUCTION BY THE CHAMBER PROCESS

In the contact process (Fig. 5) a dry gas mixture containing 7-10% sulphur dioxide and 11-14% oxygen is passed over a solid catalyst to form sulphur trioxide. The

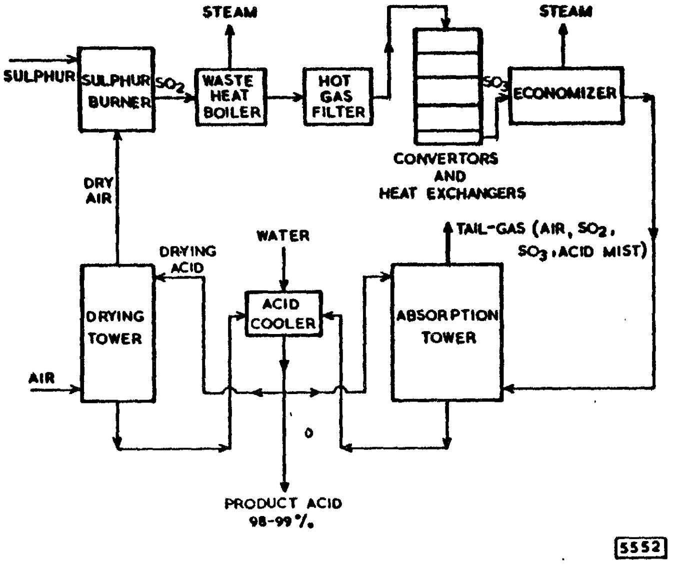


FIG. 5 FLOW SHEET FOR SULPHURIC ACID PRODUCTION BY THE CONTACT PROCESS

catalyst may be platinum or vanadium pentoxide activated with potassium. The latter catalyst is more resistant to poisoning and is generally used for the commercial oxidation of sulphur dioxide. The inlet gas temperature is controlled at about 430°C, the optimum temperature depending upon the quantity and quality of the catalyst and the composition and flow rate of the gas. Converters usually incorporate up to four stages or passes, each stage consisting of horizontal beds of catalyst with gas cooling between stages. The conversion efficiency of sulphur dioxide depends upon the number of stages and the incoming concentration of sulphur dioxide. Efficiencies between 95 and 98% are usual. The sulphur trioxide is absorbed in concentrated sulphuric acid (98.3-98.5%) in an absorption tower. Absorbing acid is continually recirculated through an external cooler, with addition of water or dilute acid to maintain the concentration. Exit gases from the absorption tower usually pass directly to the stack.

Sources of Pollution

In sulphur-burning plants for both processes, the only major continuous source of pollution is the tail-gas. Pyrites-roasting plants produce additional effluents which will be described separately. When the raw material is solid sulphur or pyrites, windage and washage may cause losses of between 1 and 2% from storage piles[37]. When liquid sulphur is used these losses are eliminated.

The Chamber Process

A survey of emissions from chamber plants has been published[37]. Although it refers to the USA, the general conclusions are likely to apply equally to plants in Europe. The primary source of emissions, which include nitrogen oxides, sulphur dioxide and acid mist, is the final Gay Lussac Tower.

Conversion efficiencies for sulphur dioxide can be higher than 98% but may be lower when raw materials other than sulphur are used. Emissions from two chamber plants[37] are shown in Table 12. Concentrations of sulphur dioxide and oxides of nitrogen fall in the range 1000-2000 ppm by volume. At least 50% of the nitrogen oxide

TABLE 12. - Atmospheric Emissions from Chamber Plants

Pollution	Concentration	Rate of Emission, kg/tonne of H_2SO_4
Sulphur Dioxide	870 ppm	12
	1640 ppm	14
Nitrogen Oxides (as NO_2)	1850 ppm	19
	990 ppm	40
Total Acid Mist*	0.21 g/m^3	1.0
	1.17 g/m^3	3.5

*Sulphuric acid mist containing about 10% dissolved oxides of nitrogen.

emission is in the form of nitrogen dioxide, which gives the tail-gas a red-brown colour. Note that the rates of emission of sulphur dioxide and oxides of nitrogen are not proportional to their concentrations. A recently published survey of emissions from chamber plants in France[38] gives emission data similar to those in Table 12.

Recovery equipment following the final Gay Lussac Tower is rarely employed, although it was reported[37] that in one plant water scrubbing reduced the sulphur dioxide by 40% and nitrogen oxides by 25%. Emissions to the atmosphere can be minimized by selection of raw materials, skill of operation and plant maintenance. Chamber plants are of small capacity and diminishing importance, so that their total contribution to atmospheric pollution is small.

The Contact Process

Emissions from a contact plant may contain both sulphur dioxide and sulphuric acid mist. The equilibrium concentration of sulphur dioxide in the tail-gas can be accurately predicted by thermodynamic principles, but the actual concentration achieved in practice depends upon the design of the plant and the operating conditions. Acid mist emissions are unpredictable and only operating experience can show whether mist is going to be a problem.

The oxidation of sulphur dioxide proceeds according to the reaction

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \text{..............................(1)}$$

$$\Delta H = - 46{,}980 \text{ k.cal}$$

The equilibrium constant for the reaction is given by

$$Kp = \frac{P^2_{SO_3}}{P^2_{SO_2}\, P_{O_2}} \quad \text{..............................(2)}$$

The equilibrium conversion of SO_2 to SO_3 as a function of temperature is shown in Fig.6.

Conversion is favoured by decreasing the temperature and the sulphur dioxide content of the feed gas and by increasing the pressure. Modern catalysts operate optimally at a temperature of around 430°C and the upper limit of conversion is therefore around 98.5%. If a catalyst were to be developed which could operate at 300°C it would be possible to achieve 99.97% conversion in a conventional contact plant. Although present day sulphuric acid plants operate at close to atmospheric pressure, an increase in pressure would favour both the sulphur dioxide conversion and the absorption efficiency. Calculations indicate that the optimum pressure would be 8-10 atm[39]. A pressure plant has been build in France for which an efficiency of 99.85% has been claimed[38,40].

A conventional contact plant can be designed to operate at 98-98.5% conversion, and this has been the practice in Europe since about 1950. The residual sulphur dioxide concentration in the tail-gas should be in the range 1800-2000 ppm, provided that the plant is not operated above its design capacity. Tests on plants in the USA yielded results ranging from 1300 to 5400 ppm, with a mean value of 2600 ppm[37]. The higher values probably reflect the American practice of designing for 96% conversion until comparatively recently. Concentrations of sulphur dioxide from a number of plants in Sweden were mostly in the range 1500-2000 ppm[12]. According to a comprehensive survey[38] emissions from most contact plants in France fall in the range 1000-2500 ppm, with a mean value of 1800 ppm. At a conversion efficiency of 98% a sulphuric acid plant will emit 13 kg of sulphur dioxide per tonne of acid produced.

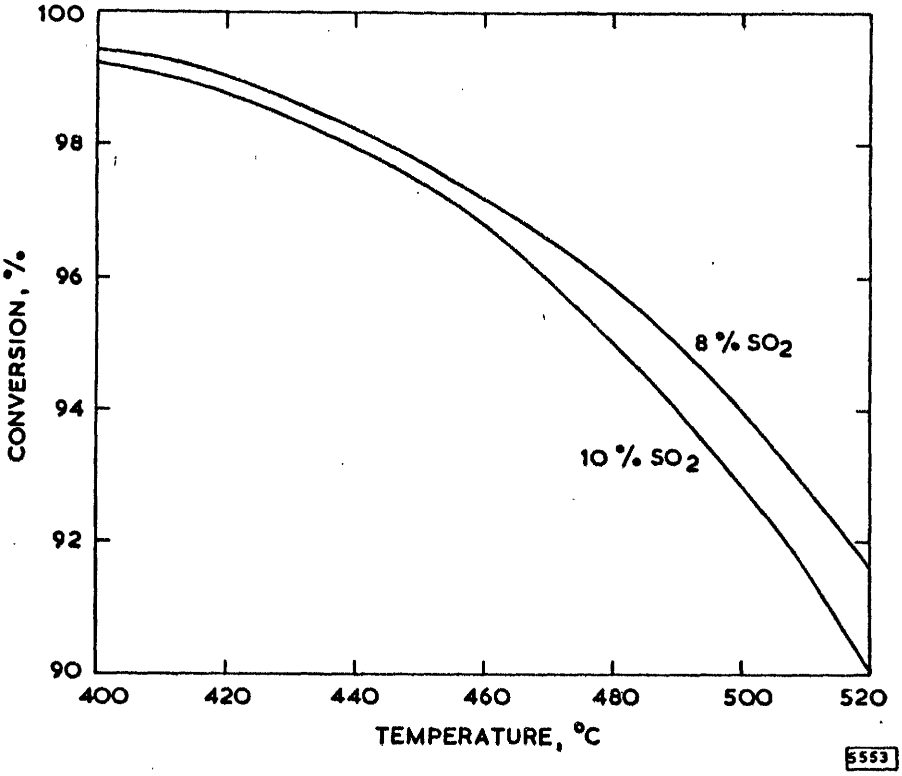


FIG.6 EQUILIBRIUM CONVERSION OF SO_2 TO SO_3 AS A FUNCTION OF TEMPERATURE

Sulphuric acid mist consists of small droplets of sulphuric acid formed in the vapour phase in the absorption tower by the reaction between sulphur trioxide and water. It is thought that nitrogen fixation in the plant might contribute to acid mist formation due to the reaction between nitric oxide and sulphur dioxide to form sulphur trioxide in the absorption tower. The mist is extremely stable and not easily removed. The vapour pressure of sulphuric acid goes through a minimum at 98.3-98.5% concentration, so this concentration of acid is used in the absorption tower in order to minimize mist formation. Precautions are taken to keep water our of the plant, but it may be present due to inadequate performance of the drying tower, moisture in the sulphur or the presence of hydrocarbons in the sulphur which form water on combustion. The mode of formation of mist is not completely understood and contractors will not guarantee freedom from mist unless filters are installed.

In the survey of plants in the USA[37] concentrations of acid mist were normally between 105 and 525 mg/m^3 but values as low as 35 mg/m^3 and as high as 1750 mg/m^3 were observed. The rate of acid mist emission in most plants without control equipment was in the range of 0.3-1.7 kg per tonne of product, but values as high as 5-7 kg were reported from some plants. The presence of a dense white plume at the absorber stack exit indicates the presence of small particles (i.e. less than 3×10^{-3} mm in diameter). The concentration of unabsorbed sulphur trioxide varied between 17.5 and 1680 mg/m^3, but was usually closer to the lower figure. Combined concentrations of acid mist and sulphur trioxide varied between 400 and 4000 mg/m^3 in the Swedish survey[12]. The corresponding rate of emission varied between 0.7 and 6.0 kg per tonne of product acid. In addition to the mist problem the sulphuric acid in the absorption tower has a vapour pressure which corresponds to a concentration of 100 mg/m^3. The sulphuric acid industry claims that only the mist leads to a white plume.

Start-up of a plant will result in increased sulphur dioxide emissions if the temperature of the catalyst is below normal working temperature. Facilities are therefore provided to pre-heat the catalyst by burning a fuel in the sulphur burner, or to pre-heat the incoming air in a pyrites-roasting plant. In this way emissions during start-up can be kept in the same range as during normal operation. For maximum absorption efficiency the absorber acid must be at a temperature of 70-90°C[39]. At lower temperatures emissions of sulphur trioxide and acid mist will be considerably higher than normal. The absorber acid is usually pre-heated for about one hour using the hot sulphur trioxide gas produced in the catalyst chamber. During this time acid mist emissions can be expected to be above normal unless some sort of mist control equipment is fitted to the plant.

Sulphuric Acid Production from Smelter Gas and Pyrites Roasting Plants

During the 1960's there was a trend away from the production of sulphuric acid in ore roasting plants (also known as metallurgical, or wet-gas plants). This is because the capital cost of a metallurgical plant can be two to three times as high as a sulphur burning plant, and they have much greater operating problems. The plant is therefore most likely to be economically viable when there is a cheap local supply of ore; or the sulphuric acid is produced as a by-product from the gas produced in the smelting of sulphide ores of such metals as lead, zinc and copper. In the latter event the sulphuric acid production provides a means of avoiding a serious air pollution problem. In France, Holland and the UK over 70% of sulphuric acid production is from sulphur-burning plants, but pyrites and smelter gas plants are still predominant in Belgium, Italy and Germany.

In metallurgical plants the gases sent to the converter contain about 7-9% sulphur dioxide. The gases will contain large quantities of suspended solids, water vapour, and possibly metallic vapours such as arsenic, lead or zinc. There will also be some sulphur trioxide resulting from the catalytic oxidation of sulphur dioxide by the iron oxide. When the gases are cooled this leads to the formation of sulphuric acid mist which can lead to increased corrosion in the cool parts of the system. A gas purification system of considerable complexity is therefore required to clean the gases before conversion to sulphur trioxide. A typical system will include cyclones to remove entrained dust, possibly an electrostatic precipitator if the metallurgical value of the dust is substantial, a scrubbing system using recirculated dilute sulphuric acid and an electrostatic precipitator to remove acid mist.

An ore-roasting plant will therefore have an additional effluent stream of weak sulphuric acid (scrubber acid) which will amount to 1-5% of the total acid production. A typical composition[41] of the scrubber acid from a pyrites plant is:

Sulphuric acid	15-30 weight per cent
Soluble iron	10-20 g/l
Solids	1-10 g/l
Chlorides	1-2 g/l

More than 60% of the solid content is iron oxide, and there will be minor quantities of elements such as selenium, zinc, lead, arsenic, copper, nickel, cobalt and calcium.

The scrubber acid has been used for the manufacture of ordinary superphosphate, or disposed of with the plant waste water. With decreasing use of superphosphate and increasing sulphuric acid production, however, a difficult disposal problem has arisen as pollution control imposes increasing restrictions on waste water composition. The acid can be purified by crystallizing the iron sulphate and concentrating by evaporation. This method has been used in Europe and Japan but it can be very expensive. In Finland scrubber acid has been used in the manufacture of complex NPK fertilizers[41]. The resulting fertilizer has a higher than normal iron content, resulting in a slightly lower water soluble phosphate level.

The deposited solids will consist of oxides of iron, lead, zinc, arsenic etc., and this may pose a disposal problem. There will also be cinder from the roaster amounting to about 75% by weight of the acid produced.

Control Techniques

By far the most important and widely used method of reducing sulphur dioxide emissions at the present time is to use the 'double contact' process (also known as double catalysis, double absorption or interpass-absorption). The process does not control acid mist emissions and separate control equipment may be necessary. Various methods of tail-gas treatment have been suggested, but none has achieved widespread commercial exploitation. Only one high pressure plant has been built and it is perhaps too early to judge its success relative to the double contact process.

Dispersion

Until recently the only method of control applied to the emission of sulphur dioxide and acid mist from a contact sulphuric acid plant was dispersion by a chimney. Dispersion into the atmosphere from a sulphuric acid plant is not very good because of the relatively low temperature of the tail-gas[42]. Table 13 shows the chimney heights recommended by the UK Alkali Inspectorate[20] for plants operating at an efficiency of 98%.

TABLE 13. - Recommended Chimney Heights for Sulphuric Acid Plants

Production Tonnes H_2SO_4 per day	Chimney Height	Production Tonnes H_2SO_4 per day	Chimney Height
200	138 ft (42m)	1200	340 ft (103m)
400	197 ft (60m)	1400	367 ft (112m)
600	241 ft (73m)	1600	394 ft (120m)
800	278 ft (85m)	1800	418 ft (127m)
1000	310 ft (93m)	2000	439 ft (134m)

The Double Contact Process

Although the principle of the process was proposed as long ago as 1901, the first double contact sulphuric acid plant was built in Germany in 1964[42]. The process is based upon the fundamental principle that, under equilibrium conditions, the yield of a chemical reaction can be increased by removing the product from the reaction. The sulphur dioxide and oxygen pass through two or three catalyst beds in a conventional reactor. They are then cooled and the sulphur trioxide is absorbed in an intermediate absorption tower. About 90% of the sulphur dioxide is converted in the first stage so that the residual gas has a very high oxygen to sulphur dioxide ratio. This gas is reheated and conveyed to a further catalyst bed and, the system being far from equilibrium, further sulphur dioxide reacts so that a very high overall conversion efficiency is achieved. It is also possible to operate the first stage at a higher sulphur dioxide concentration than in a conventional contact plant. The first commercial-scale trials showed that an initial sulphur dioxide concentration of up to 13.4% could be used[42].

Theoretically the double contact process allows an efficiency of up to 99.8% to be achieved. The activity of the catalyst declines slowly, however, and for continuous running a mean efficiency of up to about 99.5% can be expected. This implies a sulphur dioxide concentration of around 500 ppm in the tail-gas. It would probably be regarded as economically impracticable to run a double contact plant continuously at sulphur dioxide levels much lower than 500 ppm because catalyst loading and consequent power consumption would rise appreciably. A considerable number of these plants have been built, both within and outside the EEC, and the technology is well established. In the UK 'best practicable means' for new sulphuric acid plants is now based upon the performance of double contact plants, although this does not preclude the use of other methods to reach the same emission level[43]. In the USA a modified double contact process has been patented for which it is claimed that a conversion efficiency of greater than 99.97% (<100 ppm SO_2) can be achieved[44], but there are no installations of this type in Europe.

The double contact process requires an additional heat exchanger and absorption tower and these will add to the capital cost of the plant. To some extent this cost is offset by the increased sulphur recovery in the product and smaller plant dimensions, because of the possibility of using a higher sulphur dioxide concentration. In Germany, in 1968, it was claimed that the cost of sulphuric acid was not increased[42], but at the present time comparatively low sulphur prices mean that sulphuric acid production by the double contact process is more expensive.

Table 14 summarizes some estimates of the cost of sulphur dioxide control by use of various types of double absorption system under American conditions[45,46]. These costs correspond to increasing the efficiency of the process from 96% to 99.5%, rather than from 98% as would be the case in Europe. The value of the additional sulphuric acid production will therefore be greater and the net cost of control quoted in Table 14 will be smaller than the cost of applying similar control methods to European plants. This can be illustrated by carrying out a rough calculation of the extra cost of producing sulphuric acid in a double contact plant under UK conditions. The capital increment for a double contact plant is about 15%, or more if the double absorption unit is added to an existing plant. The capital cost of a large double contact plant amounts to around £2000 per daily tonne of acid for plants of 700-1000 tonne/d capacity, which is the range in which new plants are being built. An approximate calculation

TABLE 14. - Control Costs for Various Double Contact Processes

Type of Plant	SO_2 Control Cost, $/tonne		
	230 tonne/d	680 tonne/d	1350/tonne/d
New S-burning Double-Contact	0.45	0.20	0.13
Add-on systems using heat exchange with existing plant	0.80-1.50	0.55-1.05	0.50-0.80
Add-on system with outside heat source	2.50	-	-

balancing the 1½% decrease in sulphur usage (£13/tonne) against the increased capital charges (at 30% per annum) gives a figure of £0.17 ($0.42) for the additional cost per tonne of sulphuric acid produced by the double contact process.

Comparison with the appropriate figure in Table 14 shows that the costs quoted in this table are probably too low by a factor of two.

Schemes have been published for the addition of equipment to convert a conventional contact plant to double absorption[44,47]. Such conversions are rare because it is likely to be very difficult to find space for the additional equipment, modifications to the heat exchange system of the existing plant may be necessary, and in the absence of retroactive legislation there is little incentive to carry out the conversion. Costs are quoted in Table 14 for two types of add-on double absorption system, viz. add-on systems which use heat exchange facilities with the existing plant and add-on systems which use an outside heat source to raise the temperature of the gases from the primary absorption tower to the reaction temperature in the secondary converter. The latter system would probably be required in a metallurgical plant where there is no usable excess heat available. Not surprisingly the cost of control in an add-on system is higher than in a new double contact plant.

Tail-Gas Treatment

If continuous control of sulphur dioxide emissions to less than 200 ppm is required, then it seems likely that some form of tail-gas treatment will be necessary. Numerous scrubbing systems to reduce sulphur dioxide emissions have been proposed, many of which are primarily designed for desulphurization of power plant flue gases. Only a few of these systems have been applied to sulphuric acid plants but those processes which recover sulphur dioxide for recycle to the plant should be particularly attractive to sulphuric acid manufacturers.

In Europe the Lurgi Sulfacid Process[48] has been developed, and ammonia scrubbing has found commercial application. The former process uses sorption and oxidation of sulphur dioxide in charcoal beds to produce weak (10%) sulphuric acid. A 200 tonne/d plant in Toulouse uses ammonia scrubbing to recover 90% of the sulphur from the tail-gas i.e. 400 tonnes/y, one third as 98% sulphuric acid and two thirds as concentrated ammonium sulphate solution[49]. Ammonium sulphate is today a relatively undesirable by-product and problems of disposal or sale have therefore limited the application of ammonia scrubbing. A process in operation in Rumania[50] avoids the disposal problem by stripping the sulphur dioxide from solution with phosphoric acid. The sulphur dioxide is returned to the sulphuric acid plant and the ammonium phosphate is used in a complex fertilizer plant. A similar process in Czechoslavakia uses nitric acid for sulphur dioxide regeneration and yields a dilute solution of ammonium nitrate.

In the USA the Wellman-Lord (Davy-Powergas) process has been applied to sulphuric acid plants. In this process the sulphur dioxide is absorbed in sodium sulphite solution to form sodium bisulphite and subsequently regenerated from the circulating solution. A small amount of the solution is oxidized to non-regenerable sulphate and this must be bled off for disposal.

In addition to problems of by-product disposal, aqueous scrubbing processes have an additional disadvantage. There will be a tendency to cool the tail-gas plume so much that it will have very little buoyancy so that ground level sulphur dioxide concentrations in the vicinity of the plant might be no lower than they would be in the absence of treatment.

A detailed survey of the economics and feasibility of sulphur dioxide recovery schemes has been carried out in the USA by the Chemico Company[45,46]. Estimated costs for the most promising processes are given in Table 15.

The costs quoted in the Table were calculated for plants built in the USA in 1970 but they have been converted into dollars per tonne of sulphuric acid. They can be regarded only as approximate because the cost per tonne of sulphuric acid for pollution control for each process would depend on local circumstances. In particular the cost of sulphur and the credit assigned to by-products can vary considerably. Nevertheless they do provide a useful guide for comparing the double contact process with tail-gas treatment. The incremental cost per tonne of acid for a new double contact plant was estimated in the same survey to be $0.45 for a 230 tonne/d plant and $0.13 for a 1350 tonne/d plant (see Table 14). The cost of tail-gas treatment is therefore very high in a small plant, and even in a very large plant it is likely to be significantly higher than for double absorption.

A molecular sieve system for sulphur dioxide recovery has been installed on a 180 tonne/d sulphuric acid plant in the USA[35]. In the first three months of operation a sulphur dioxide concentration in the tail-gas of 15-25 ppm has been achieved, corresponding to less than 0.2 kg/tonne of acid produced. The capital cost of the equipment was $397,000 and the net treatment cost was estimated to be $2.23/tonne of product. It remains to be seen whether the high performance of this plant can be sustained in long term operation.

Mist Eliminators

It has already been pointed out that acid mist carry-over can be minimized by careful control of conditions in the absorption tower. The unpredictable nature of mist formation means, however, that control equipment must be installed to ensure that very low quantities of mist are discharged under all conditions of operation. A detailed comparison of the available systems for mist control has been given[46]. The efficiencies and costs of the various systems are compared in Table 16.

TABLE 15. – Summary of Estimated Costs of Selected Potential Processes to Control Sulphuric Acid Plant Emissions to below 200 ppm SO_2

Process Description	Costs for 230 tonne/d Plant		Costs for 1350 tonne/d Plant	
	Capital (\$1 000)	SO_2 Control (\$/tonne of acid)	Capital (\$1 000)	SO_2 control (\$/tonne of acid)
Scrubbing with Na_2CO_3 solution, crystallization and sale of Na_2SO_3 crystals	570	3.30	-	-
Scrubbing with MgO slurry, calcination to recover MgO for recycle to scrubber and SO_2 for recycle to the acid plant	470	3.20	1 040	0.80
Scrubbing with K_2SO_3 solution, precipitation of $K_2S_2O_5$ stripping to recover K_2SO_3 for recycle to the acid plant	580	2.90	-	-
Scrubbing with methyl ammonium sulphite solution, stripping to recover $(CH_3NH_3)_2$ SO_3 for recycle to the scrubber and SO_2 for recycle to the acid plant	450	2.90	2 080	0.90
Sorption and oxidation of SO_2 in charcoal beds, production of weak sulphuric acid (Lurgi Sulfacid process)	No cost estimates made			
Scrubbing with lime slurry, disposal of $CaSO_3.CaSO_4$ sludge	260	2.75	570	1.00
Scrubbing with aqueous ammonia, treatment of scrubbing solution with nitric acid to recover SO_2 for recycle to the acid plant with NH_4NO_3 for sale	600	3.10	-	-

TABLE 16. - Efficiency and Cost of Acid Mist Eliminators

Process	Efficiency $>3 \times 10^{-3}$ mm	Efficiency $<3 \times 10^{-3}$ mm	Emission Level* mg/m^3	Capital Cost for System on New Sulphur Burning Plant in $\$ \times 10^3$		
				230 tonne/d	680 tonne/d	1350 tonne/d
Horizontal Mesh Pads	>99%	15-30%	up to 70	20	28	38
Glass Fibre Packed Vertical Tubes (High Efficiency)	100%	95-99%	3.5	70	105	170
Vertical Fibre Panels (High Velocity)	100%	90-98%	17.5	23	55	95
Electrostatic Precipitation	99%	nearly 100%	17.5	85	105	200

*Figures based on manufacturers specifications

The principle of the first three methods in Table 16 is the formation (from the mist) of large droplets which return to the absorption tower by gravity. The least expensive method uses horizontal pads of stainless steel or teflon mesh supported on a stainless steel grid. This method is not effective for very small droplets but high efficiency for droplets less than 3×10^{-3} mm in diameter can be achieved with glass fibre mist eliminators[51]. The latter are easily installed, require very little maintenance, and the only operating cost is the power required to overcome the very small pressure drop across the separator. Electrostatic precipitators are also very efficient, but they are less popular because they are expensive, bulky, and difficult to install, operate and maintain[39].

The emission levels quoted in Table 16 are based upon mist control equipment manufacturers' specifications and are probably optimistic. A contractor with considerable experience in building sulphuric acid plants has quoted emission levels of 35 mg/m^3 of acid mist for the high efficiency type fibre mist filters, and 70 mg/m^3 (which is equivalent to about 0.075 kg/tonne of sulphuric acid) for the high velocity type. The former would cost about 2% of the capital cost of the plant or £20 000 ($50 000) for a 1000 tonne/d plant, the latter about 1%. Filters would be fitted in both absorption towers of a double contact plant in order to minimize the risk of corrosion due to carry-over of mist from the intermediate absorption tower. The cost of producing sulphuric acid would be increased by a small amount, less than $0.05/tonne.

Summary

A conventional contact process sulphuric acid plant is capable of a sulphur dioxide conversion efficiency of up to 98%. The new double contact process enables conversion efficiencies greater than 99.5% to be achieved. Sulphur dioxide concentrations of less than 500 ppm can be expected in the tail-gas from a double contact plant. An increase of about 15% in the capital cost of the plant is likely, which is only partially offset by the higher conversion efficiency. Lower sulphur dioxide emission levels can be achieved by various tail-gas scrubbing processes but there are several disadvantages to these processes and the cost is likely to be relatively high. Acid mist carry over can be controlled effectively by means of fibre mist eliminators.

PHOSPHORIC ACID AND SUPERPHOSPHATE

Process Descriptions

Phosphoric Acid

The starting material for phosphoric acid manufacture is phosphate rock which exists principally as the mineral francolite, carbonato-fluorapatite $Ca_{10}F_2(PO_4)_6$ x

$CaCO_3$ and in minor amounts as chlorapatite and hydroxyapatite. Most phosphate rock used in phosphoric acid manufacture comes from sedimentary deposits formed by reprecipitation of dissolved phosphate from prehistoric seas. The principal exception is Kola apatite, an igneous type mined in northern Europe. The rock contains numerous impurities, of which the most important are silicates and iron and aluminium oxides. Two general methods are available for processing the rock, the wet process and the furnace process.

In the furnace process, phosphate rock is fused with coke and silica in an electric furnace. Elemental phosphorus is produced, which can then be converted to phosphoric acid. A high purity acid is produced which is essential for some applications. An example is the manufacture of detergents, although purified wet process acid is also used. The lower purity acid produced by the wet process is adequate for fertilizer manufacture. The furnace process involves high power costs and is therefore of no significance for fertilizer manufacture in the EEC. This is in contrast to the USA, where furnace acid is used to produce superphosphoric acid (70% P_2O_5)* which is used in the production of liquid fertilizers. It is estimated that about 5% of the phosphoric acid production in the EEC is by the furnace process, produced in plants in France, Germany and Italy[52]. Production in the UK ceased in 1970.

In the wet process, finely ground rock is treated with a strong mineral acid, normally sulphuric, followed by separation of the precipitated calcium sulphate. The overall reaction can be sub-divided into three simplified steps.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4 \quad \text{.......} (1)$$

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 \quad \text{.......} (2)$$

$$CaCO_3 + H_2SO_4 \rightarrow CO_2 + CaSO_4 + H_2O \quad \text{.......} (3)$$

The hydrogen fluoride produced may react with silica to product silicon tetrafluoride which then hydrolyses to fluorosilicic acid:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \quad \text{.......} (4)$$

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2 \quad \text{.......} (5)$$

The precipitated calcium sulphate can be in three stages of hydration depending upon the temperature and the phosphoric acid concentration. The three forms are:

anhydrite	$CaSO_4$
hemihydrate	$CaSO_4.\frac{1}{2}H_2O$
dihydrate	$CaSO_4\ 2H_2O$

---

*Concentrations of phosphoric acid are noramlly expressed in terms of weight per of P_2O_5.

Modern wet process phosphoric acid technology has concentrated upon the development of processes which produce crystals of calcium sulphate which wash and filter well, and this requires that the crystals be large, well-formed, and in a narrow particle size range. Commercial processes fall into one of three basic types which produce and separate dihydrate or hemihydrate crystals, or grow one of these two forms and convert to the other before separation.

Dihydrate processes are the most common. Direct attack of the rock with sulphuric acid is avoided, because this can coat the rock with insoluble sulphate. Dissolution takes place in a circulating phosphoric acid stream to which sulphuric acid is added. The usual conditions are 68-78°C and a phosphoric acid concentration of 30-32% P_2O_5 with 1.5-2.5% excess H_2SO_4. It is difficult to grow good calcium sulphate crystals in the dihydrate mode if the acid concentration is higher than 33% P_2O_5, but higher concentrations are possible in hemihydrate processes. A number of recent developments in phosphoric acid technology, particularly in Japan, have concentrated upon precipitation of the $CaSO_4$ in the hemihydrate form, and then conversion of the hemihydrate to dihydrate in a separate section. In this way losses of P_2O_5 in the gypsum can be considerably reduced. The recently developed Central-Prayon process achieves 99% recovery of P_2O_5 by the reverse procedure, i.e. by producing dihydrate crystals which are subsequently converted to hemihydrate. Finally mention should be made of the new Fisons process which produces stable hemihydrate crystals which can be washed on the filter without reversion to the dihydrate form. The process operates at 100°C and 42-45% P_2O_5, concentrations of up to 55% P_2O_5 are feasible. The need for concentration of the product acid can be eliminated in this way. The efficiency of the process can be increased from about 94% to 98.5% by addition of a second stage in which the hemihydrate is recrystallized to dihydrate.

A simplified flow diagram of a dihydrate process is shown in Fig. 7, which notes potential pollution sources. Crushed phosphate rock is digested in a series of agitated vessels or compartments. The slurry passes from the last compartment to a continuous rotary filter where the gypsum is separated, washed to recover weak acid and then

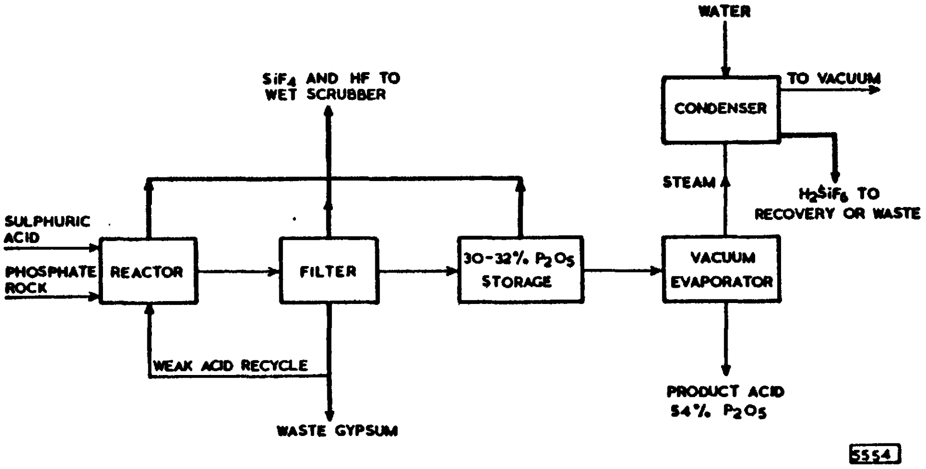


FIG. 7 FLOW SHEET FOR THE PRODUCTION OF WET-PROCESS PHOSPHORIC ACID

discharged to waste. The filtrate can be concentrated in evaporators to a final strength of up to 50-55% P_2O_5.

Superphosphates

Normal or single superphosphate has been manufactured for over 100 years. It is produced by the reaction between phosphate rock and sulphuric acid but no attempt is made to remove the calcium sulphate. Early processes used a batch method but modern plants are designed for continuous production. Sulphuric acid and pulverized rock are metered continuously to a mixer and then introduced into a continuous den. The mixture quickly solidifies and is moved as a continuous block to the opposite end of the den where it is cut into small particles. The retention time in the den is of the order of 30 minutes. The product is conveyed to a storage pile where it is stored until the chemical reactions go to completion. Simplified equations for the reactions which take place are:

$$3[Ca_3(SO_4)_2]\ Ca\ F_2 + 7\ H_2SO_4 \rightarrow 3\ [Ca\ (H_2PO_4)_2] + 7\ CaSO_4 + HF \ \ldots\ldots\ldots\ldots\ (1)$$

$$4\ HF + SiF_2 \rightarrow SiF_4 + 2H_2O \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

Single superphosphate contains only 16-21% P_2O_5. A more concentrated product, triple superphosphate containing 40-49% P_2O_5 is made by dissolving phosphate rock in phosphoric acid. Run-of-pile triple superphosphate is made by a process which is very similar to the single superphosphate process. Phosphate rock and phosphoric acid are mixed and conveyed to a curing building via several mixers or blungers to aid contact between rock and acid. The product is then cured for 30-60 days.

Cured superphosphate can be granulated by addition of water and steam in a rotary drum granulator. Alternatively a granular product can be manufactured by spraying the slurry of rock and acid on to recycled product in a rotary drum. The granules are dried and sized by screening.

Sources of Pollution

The main problems are:

(a) dust from handling and grinding phosphate rock,
(b) P_2O_5 losses in the filter cake,
(c) evolution of fluorides during digestion of rock and concentration of
    30% P_2O_5 acid,
(d) disposal of by-product gypsum.

Dust and fluoride evolution are common to phosphoric acid and superphosphate manufacture. By-product gypsum arises only in the manufacture of phosphoric acid by the wet process. Carbonates in the rock will be decomposed with the evolution of carbon dioxide but this is not considered to be a problem as far as air pollution is concerned.

Dust

Dust contains 3-4% water insoluble fluoride which appears to have little or no effect on human beings, animals or plants. It is, however, a nuisance which can be controlled by proper precautions to a loss of less than 0.1% by weight. Ground rock should always be handled and stocked in air-tight surroundings and air circulation to the atmosphere should be via dust filters. Air from the pneumatic handling system in the mills is also filtered before passing to the atmosphere.

P_2O_5 Losses

Losses of P_2O_5 in the filter cake can occur in three ways. Phosphate rock particles may become coated with impervious calcium sulphate, which prevents the reaction going to completion. Phosphate may be occluded in the calcium sulphate lattice as HPO_4^{2-} ions which are isomorphous with SO_4^{2-} ions. Incomplete washing of the filter cake gives rise to the third source of loss.

Losses due to undecomposed rock can be minimized by fine grinding of the rock. In practice the degree of fineness is determined by the grinding capacity and economics of grinding versus the value of the increased P_2O_5 recovery. Losses from this source are greater when excess sulphuric acid is present.

Occlusion of P_2O_5 in the calcium sulphate lattice is most severe at low temperatures, low sulphuric acid excess and high P_2O_5 concentration of the solution. The occluded HPO_4^{-2} ions can be retrieved only by destroying and reforming the lattice in the presence of an excess of sulphate ions. The P_2O_5 efficiency in a conventional dihydrate process seldom exceeds 95%, but up to 99% efficiency can be achieved in processes which include a recrystallization stage.

Filtration loss is determined largely by the size and shape of the calcium sulphate crystals. In dihydrate processes the most easily filterable crystals are often obtained when the sulphuric acid is present in an excess of about 1½-2%. The extent of washing is limited by the ultimate dilution of the product. In practice filter cloths tend to become gradually blocked by small crystals so that P_2O_5 losses increase. The period between changes of filter cloth is determined by a balance between the cost of shutting down the plant and the increased product recovery with a new cloth.

The gypsum filter cake can contain up to 1% insoluble P_2O_5 as well as soluble P_2O_5 from inefficient washing.

Fluorides

Most phosphate rocks contain between 3 and 4.5% by weight of fluorine. In phosphoric acid manufacture 40-60% of this is released in the form of gas during digestion of the rock and concentration of the acid. This can give rise to serious air pollution problems and consequently measures must be taken to control fluoride emissions. The fluorine is usually in the form of silicon tetrafluoride, SiF_4.

The quantity of fluoride discharged to the atmosphere can be very small in phosphoric acid manufacture because efficient control techniques have been developed. A phosphoric acid plant with modern air pollution control equipment will discharge as little as 0.02 kg of fluorides per tonne of P_2O_5 produced; as little as 0.01 kg has been reported for large plants. This should be compared with amounts greater than 1 kg per tonne of P_2O_5 which have been quoted for superphosphate manufacture[53]. Here the fluoride which escapes to the atmosphere is evolved mainly from the curing pile where temperature control is commonly difficult, and the large quantities of air involved hinder the collection and scrubbing of the diffused gases. Fluoride emissions from the mixer and den can be controlled more easily. It should be noted, however, that in controlling air pollution by wet scrubbing a considerable water pollution problem may arise.

Fluorine Distribution in Phosphoric Acid Manufacture

The fluorine released from the rock will be distributed between the acid product, the precipitated gypsum, and the gaseous effluents. The distribution depends upon the composition of the rock and the process used. The principal factors which influence the distribution are[39].

(a) Sodium and potassium in the rock tend to precipitate fluorine as fluorosilicates or fluorine-aluminium-silica complexes which go with the gypsum.

(b) High reaction temperatures will tend to cause greater fluorine evolution in the gas phase.

(c) The production of more concentrated acid increases the quantity of fluorine released.

The effect of different types of rock on the fluorine distribution in dihydrate processes is shown in Table 17. The theoretical yield of fluoride from apatite is 89 kg per tonne of P_2O_5, but over 100 kg/tonne is usually obtained because of other fluorides present in the rock. In a dihydrate plant using Florida or Morocco rock around 5 kg/tonne will be released in the reactor and from 20 to 60 kg/tonne in the concentration of the acid.

TABLE 17. - Fluorine Distribution in Dihydrate Processes

Rock	Composition, %		Fluorine Distribution, % of total F					Reference
	P_2O_5	F	gypsum	reactor off-gas	weak acid	concentration	concentrated acid	
Florida	30.5-32.6	3.3-3.9	45	3	52	-	-	53
			18-30	4-6	-	35-50	25-35	54
Morocco	35.1	4.2	47	3	50	-	-	53
			25-55	5.7	-	20-40	17-30	54
Kola	40.3	3.3	15	12	73	-	-	53
			15-30	5-10	-	40-60	19-30	55
Nauru	38.9	2.6	75	2	23	-	-	53
			-	4.5	-	-	-	56

Hemihydrate processes, operating at a higher temperature, will tend to release a greater proportion of fluoride in the reactor. Data for a hemihydrate process producing 50% P_2O_5 acid using Togo rock are given in Table 18[57].

TABLE 18. - Fluorine Distribution in Hemihydrate Process

Fluorine Distribution, % of total F

	Hemihydrate	Typical Dihydrate
Product Acid	12	15
Filter Cake	50	45
Reactor Off-gases	8	5
Flash Cooler	30	-
Concentration Unit	-	40

The fluorine given off in the reactor and flash cooler amounts to about the same as the combined fluorine from the reactor and concentration unit in a dihydrate process.

Fluoride Emissions to the Atmosphere

Atmospheric emissions from wet process phosphoric acid manufacture have been described in detail in a report issued by the Environmental Protection Agency in the United States[58]. Detailed consideration to this topic has also been given by Barut and Schwob[39], and by several authors in Slack's monograph on Phosphoric Acid[53].

In the manufacture of 32% P_2O_5 acid, the most important source of fluoride emissions is the reactor, and significant amounts are emitted from filters and storage tanks. Minor amounts will be emitted from any other points in the process where there are exposed surfaces of reaction slurry or aqueous solutions containing fluorine compounds. Some data on fluorine concentrations before and after scrubbing are collected together in Table 19. There are quite wide variations in the concentration of fluorine evolved, and this is due to variations in the type of phosphate rock used and the different conditions prevailing in the various processes. Nevertheless there is reasonable agreement between different sources of information and the concentration ranges quoted are believed to be representative.

During reaction of the rock and acid the slurry must be cooled to retard corrosion and the formation of hemihydrate. The methods of cooling has an important influence on the emission of fluorides. As far as air pollution is concerned the less satisfactory method is air sparging. The off-gases are collected, mixed with fresh air and forced through the slurry. A large volume of waste gas is generated with a substantial non-condensible content, so that removal of fluorides is relatively difficult. The alternative method is vacuum cooling. Water is evaporated under vacuum and the vapour is condensed in a barometric condenser, thereby trapping evolved fluorides in the condenser water. Air pollution control is inherent in this system,

TABLE 19. - Fluride Emissions in Phosphoric Acid Manufacture

Source of Emission	Concentration of Flurides			Source of Data	Reference
	Before Scrubbing mg F/m^3	Fluorine Discharged to Atmosphere after Scrubbing			
		mg F/m^3	kg F/tonne P_2O_5		
reactor filter storage tank	32-940 5-20 8-55	2.45-33.6	0.003-0.085	16 plants in USA	58
Reactor reactor & filter	- -	- -	0.003-0.15 0.002-0.08	5 plants in Florida 7 plants in Florida	59
Not specified	-	8.5-13.0	-	plant in Rouen	60
Not specified	- -	1.5-2.0 mean 5.6	- mean 0.01	plant in France	61
Not specified	400	12	0.13	plant in Sweden	12
reactor: air cooling vacuum cooling filter storage tank	200-700 300-1000 100-200 50-100	-	0.06	not quoted	39
reactor filter, storage tanks and other losses	600-1000 10-50	10-50	-	Licensors specification	60

at the expense of creating an aqueous fluorine-bearing effluent.

Emissions of particulates can also occur in the process. Emissions of 0.1 kg/tonne P_2O_5 have been reported for filter operations, and up to 5.5 kg/tonne P_2O_5 for reactor operations. Only 3-6% of the particulate emissions consists of fluorides.

The amount of fluorine discharged to the atmosphere will depend upon the efficiency of the scrubbing system which is used. This will be discussed in a later section. It is clear from Table 19 that it should be possible to achieve an emission of less than 0.01 kg per tonne of P_2O_5 produced.

Acid Concentration

Table 17 shows that a large proportion of the fluorine in the rock is released during concentration of phosphoric acid from 30 to as high as 54% P_2O_5. If concentration is carried out by submerged combustion dilution of fluorides in the combustion gas makes scrubbing difficult. In the case of a vacuum concentration plant the fluorine is absorbed in the barometric condenser water. The concentration of fluorine can be sufficiently high for it to be economical to recover it as fluorosilicic acid in some cases.

Fluoride Emissions in Superphosphate Manufacture

Fluorides are evolved from various steps in the manufacture of normal superphosphate, mainly as silicon tetrafluoride. Overall fluoride evolution can vary between 10% and 50% of the fluoride in the rock[4]. Assuming a fluorine content of 3.5% in the rock, between 2 and 10 kg of fluorine will be released per tonne of product. Fluoride evolution is less erratic in triple superphosphate manufacture, ranging between 32% and 40% of the fluoride in the rock, or 5-6 kg/tonne of product. Typical fluoride distributions in superphosphate manufacture are summarized in Table 20.

TABLE 20. - Fluorine Distribution in Superphosphate Manufacture

Source	Single Superphosphate		Triple Superphosphate	
	% of the F in rock	kg/tonne product	% of the F in rock	kg/tonne product
Mixer	2	0.4	32	5
Den and Conveyors	30	6.0		
Storage pile (curing)	3	0.6	3	0.5
In product	65	13.0	65	10

The fluoride concentration in the off-gas streams from the mixer, den and conveyors is relatively high, e.g. a concentration gradient of 1100-8300 mg F/m^3 has been quoted for a den making 11 tonne/h of single superphosphate[63]. These streams are usually combined and scrubbed in a single scrubber system.

Fluorine emissions from a number of superphosphate plants in Florida[59] and plants in France[61] and Ireland are summarized in Table 21. The emissions fall into the same range as those from phosphoric acid manufacture, and the final amount of fluorine discharged to the atmosphere will depend upon the efficiency of the scrubber. The American results do not indicate any significant differences in fluoride emissions from the manufacture of the three different forms of product. The French results show that the fluoride emissions from the granulation plant were considerably lower than the emissions from the manufacture of run-of-pile superphosphate. The granulation plant in this case was equipped with cyclones to control dust but there was no scrubbing of gaseous fluorides. The Irish plant is fitted with a two-stage scrubbing system and fluoride emissions are very low.

TABLE 21. - Fluoride Emissions from Superphosphate Plants

Product	Fluorine Emissions to Atmosphere		Source of Data	Reference
	mg F/m^3	kg F/tonne product		
Run-of-pile TSP	-	0.04-0.24	4 plants in Florida	59
	5-50 (mean 22.5)	0.2	plant in France	61
Granular TSP from cured run-of-pile	-	0.03-0.23	5 plants in Florida	59
	3-30 (mean 15)	0.04	plant in France	61
Granular TSP direct granulation	-	0.02-0.8	4 plants in Florida	59
Run-of-pile SSP	10-60	0.01-0.04	plant in Ireland	-
" TSP	1-10	0.001-0.01		

Emissions from curing and storage sheds are not included in Table 21. Around 3% of the fluorine in the phosphate rock is emitted over a period of 4-6 weeks. Natural circulation of air is used for ventilation and fluoride concentrations are low. Usually no attempt is made to control this source of air pollution. In Florida it has been found that an uncontrolled curing building will contribute 0.75-1.5 kg of fluoride per tonne of product stored. The daily emissions ranged from 90 to 1600 kg [59].

Concentrations of fluorine in the atmosphere[53] varied between 34-68 mg/m^3 at the surface of the pile to 5100-7650 mg/m^3 in the centre. Air flow quantities were in the range 5700-17100 m^3/min and the concentration of fluorine in the off-gas was 105-525 mg/m^3. There have been some attempts in Florida to design storage buildings so that efficient scrubbing of the gas can be carried out[53,59].

Aqueous Effluents

The control of fluoride emissions to the atmosphere and the composition of the aqueous effluent stream from phosphoric acid and superphosphate plants are interdependent. The major source of aqueous effluent in many phosphoric acid plants is the cooling water from the barometric condenser on the concentration unit. A specification for a typical dihydrate process[62] gives the following cooling water composition for a once-through system:

P_2O_5	:	50 g/m^3
F	:	1000 g/m^3 (falls to 100 g/m^3 if fluorine recovery unit is installed)
Cl	:	100 g/m^3
Outlet temperature	:	45°C

At an inlet temperature of 20°C, 30 tonnes of cooling water are required per tonne of water evaporated, which corresponds to 40 m^3/tonne of P_2O_5. The fluoride content of this water amounts to 40 kg of fluorine per tonne of P_2O_5, falling to 4 kg if a fluorine recovery unit is installed. The P_2O_5 content of the cooling water is 2 kg/tonne of product.

This water is suitable for re-use in other parts of the plant. For example, a small amount can be used for washing the filter cake and may therefore be returned to the process. The remainder is often used to scrub the gases from the reactor, which will not add very much to the fluorine content, and then goes to slurry the gypsum for disposal by pipeline to the sea or an estuary. Using a once-through system of this type with inlet water at 20°C a 500 tonne/d plant would discharge the following approximate quantities of pollutants:

Gypsum	:	2500 tonne/d
Fluorine	:	20 tonne/d
P_2O_5	:	1 tonne/d

In addition to the fluorine in solution, the gypsum will contain approximately 20 tonne/d of fluorine, mainly as insoluble fluorosilicates and calcium fluoride.

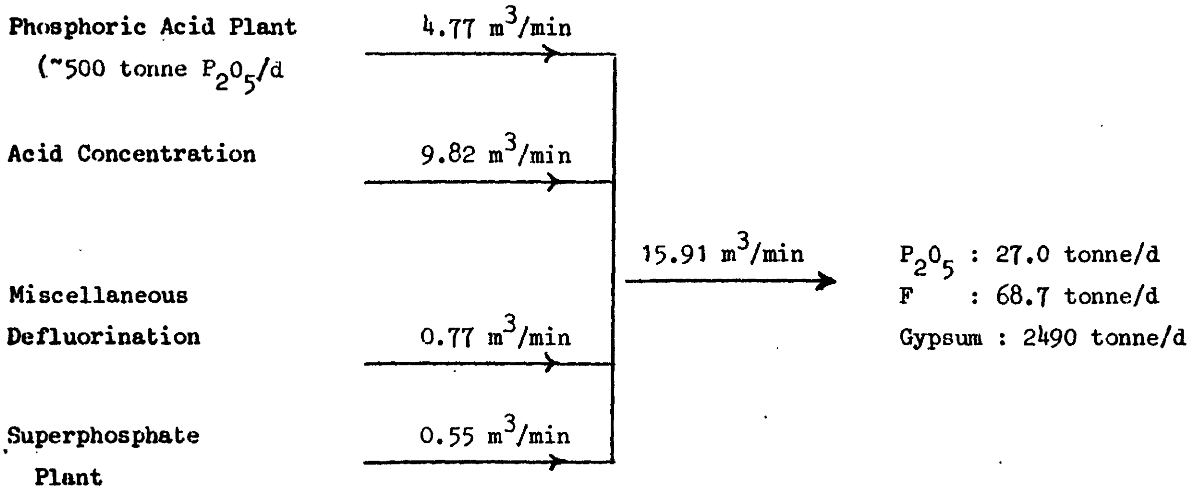
Alternatively cooling water can be re-used to minimize the quantity of liquid effluent to be discharged, using cooling ponds or towers in a closed circuit. Where recirculation is carried out, whether for fluorine recovery or for more convenient effluent disposal, it is preferable to use two stages of absorption[64]. The optimum fluorosilicic acid concentration is about 20%; the absorption rate is diminished at higher concentrations. To maintain this concentration it will be necessary to bleed off some of the liquor and a make-up of fresh water will be required. The expected analysis of the recycled water and the effluent solution which is bled off would be:

F : 1000-2000 g/m^3
P_2O_5 : 200-500 g/m^3

In a closed circuit system the cooling water can be used to slurry the gypsum so that it can be pumped to a settling pond. This system, very popular in the USA, is not extensively used in Europe.

The quantity of aqueous effluent from a superphosphate plant will be very much smaller, i.e. up to about 1 m^3/tonne P_2O_5[4]. This stream will contain most of the fluorides which were evolved in the mixer and den and then scrubbed for air pollution control. The scrubber liquor from one plant contains phosphorus and fluorine at concentrations of 340 g/m^3 and 1100 g/m^3 respectively.

There is one published report on the overall aqueous effluent from a phosphate fertilizer complex, situated in Canada[65]. The following rates of flow of water were quoted:



The capacities of the plants were not quoted but the quantity of gypsum implies that the capacity of the phosphoric acid plant must be about 500 tonne/d. With the exception of the P_2O_5 content the above figures are all of the same order of magnitude as those quoted previously. By installing a total recycle system in the plant the total flow of water from the plant was reduced from 15.91 m^3/min to 0.9 m^3/min.

Fluoride can be removed from the aqueous effluent by treating with lime, but the quantity of lime needed is high (300 kg of CaO/tonne of P_2O_5). In many plants the effluent is simply diluted with cooling water, mixed with other effluent streams and discharged.

Control of Gaseous Effluents and Fluorine Recovery

The operation of wet scrubbers for control of gaseous fluoride emissions is complicated by the precipitation of silica in the scrubber. The amount of silica precipitated depends upon the form in which the fluorine is released. In the reactor it is usually SiF_4. Scrubbing of SiF_4 with water results in the formation of fluorosilicic acid, H_2SiF_6*.

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$$

If the washing temperature is below 50°C, silica is precipitated as a gel which will stick to most surfaces, such as fan blades or packing. At higher temperatures hard granules are formed which may be cemented together, so that encrusting can again be a serious problem.

In the concentration unit fluorine is released as a mixture of SiF_4 and HF. The ratio of HF : SiF_4 depends upon the P_2O_5 content of the acid and the silica content of the rock from which the acid was made. Sometimes silica is added to diminish HF production in favour of SiF_4, to minimize corrosion problems.

In the case of Florida rock:

$$HF : SiF_4 < 2 \text{ for } P_2O_5 < 50\%$$

$$HF : SiF_4 > 2 \text{ for } P_2O_5 > 56\%$$

It follows that in the concentration from 30% to 54% P_2O_5 the fluorine is released in such a way that the solution is practically all H_2SiF_6. Concentration to 45% releases a greater proportion of SiF_4 so that gelatinous silica is precipitated. In the latter case the washing plant must be fitted with a system for filtration of the silica.

Results of tests on a number of different scrubber systems[58] are shown in Table 22. Simple void spray towers are relatively inexpensive to build, the pressure drop is low, and they are not subject to much trouble from plugging by silica. The maximum absorption efficiency of a single unit can be up to 75-80%[64] but the efficiencies quoted in Table 22 are somewhat lower. It is necessary to use several units in series if higher efficiencies are required. Cyclonic spray scrubbers have been popular as a result of their simple design. Table 22 indicates that efficiencies of up to 95% are possible, but a higher pressure drop is required for cyclonic scrubbers than for void scrubbers.

In the USA the spray cross-flow packed scrubber is considered to be the best control device available for fluoride emissions. It consists of two sections, the first of which is an open spray chamber. Silica is precipitated in this section and

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*Fluorosilicic acid is the name approved by I.U.P.A.C., although fluosilicic acid is used more frequently.

TABLE 22. - Efficiency of Wet Scrubbers for Fluorine Removal[58]

Type of Scrubber	Efficiency, %	Fluorides emitted from Scrubber	
		mg F/m^3	kg F/tonne P_2O_5
Simple Void Spray Tower	57-72	173-207	0.26-0.30
Cyclonic Spray Tower	90-95	3.7-6.8	0.024-0.041
Spray Cross-flow Packed	57-99.9	2.3-32	0.003-0.08
Impingement Scrubber	15-62	4.6-8.5	0.003-0.005
Venturi	84-96	24-53	0.013-0.019

the gases proceed to a packed section for removal of the remaining fluorides. Gases low in fluorides, such as those from the filtration unit, are sent directly to the packed section. An efficiency of 99.9% was obtained in this type of scrubber, but this was obtained with an extremely high inlet concentration of fluoride (9000 mg/m^3).

The impingement scrubber in the series of tests in Table 22 gave a lower efficiency than expected, probably because of the low inlet fluoride concentration. Venturi scrubbers are capable of high efficiency and have the advantage that they are capable of self cleaning because of the great force of the water jet. Running costs are relatively high, however, because of the high pressure drop required.

The data in Table 22 do not show any simple relationship between the efficiency of the scrubber and the concentration of fluorides discharged from the scrubber in the gas phase. This appears to be due to the effect of the inlet concentration of fluorides on the efficiency. It is therefore important not to over-emphasize the importance of scrubber efficiency. The efficiency required to give a specified level of control will depend upon the concentration of fluorides in the gases at the inlet of the scrubber.

The investment cost for a complete exhaust system, including a multi-pass void spray tower scrubber and stack capable of meeting UK regulations on the discharge of fluorides, has been estimated as £40 000 for a 180 tonne/d plant with an airflow of 103 000 m^3/h. Power and water costs would be relatively low, but capital charges would result in a running cost of £0.2 or $0.5 per tonne of P_2O_5. In plants with vacuum cooling, air pollution control is obtained without increased cost.

To meet the proposed emission standard of 0.01 kg F/tonne P_2O_5 in the USA, the Environmental Protection Agency has suggested that the spray cross-flow packed scrubber is the best control device for wet process phosphoric acid plants[66]. For typical operating conditions a fluoride removal efficiency of 99.6% is achieved at a pressure drop of 8-10 mm WG*.

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*Manufacturers and users of wet scrubbers still prefer to express pressure drops in terms of water gauge; 1 mm ≡ 9.81 N/m^2.

The capital and annual costs for installation of this type of scrubber on two sizes of plant are shown in Table 23. The capital cost includes the scrubber, fan, water circulating pumps, 37 m of duct work and a 30 m stack. All surfaces exposed to the scrubbing water are coated with polyvinyl chloride or similar corrosion resistant material. The costs are based upon a scrubber designed to use gypsum pond water as the scrubbing medium. The figures may therefore not be accurate for an installation on most European plants, but they should be of the right order of magnitude.

The cost of control is very dependent upon the volume of gas that must be treated, and this can vary considerably, even in plants of the same capacity. The plant designer has a certain amount of control over the gas volume, and can reduce the control cost by designing tighter seals around the reactor, filter and sumps. For each plant capacity in Table 23 costs are given for two gas flow-rates, one representing a "typical" gas flow-rate and the other representing a "reduced" flow-rate. Information from other sources suggests that the latter case might be more representative of recently built plants.

It can be seen from Table 23 that the capital cost is reduced by about 35% when the gas flow-rate is reduced by a factor of three. It should be noted that when the cost of utilities is subtracted from the annual cost the remainder is approximately equivalent to 30% of the total installed capital cost. The cost of control per tonne of product varies from $0.15-0.25 in a 450 tonne/d plant, and from $0.10-0.17 in a 800 tonne/d plant.

Detailed control costs have also been estimated for granular triple superphosphate plants in the USA[66]. The process considered is similar to the TVA process which is used for the production of granular compound fertilizers. The possibility of using a combination of scrubbers designed to remove particulates and fluorides respectively was considered for each stage of the process. The control system was designed to meet the EPA emission standard for fluorides of less than 0.15 kg/tonne P_2O_5. Costs were calculated for typical gas flows in model plants of 230 tonne/d and 360 tonne/d capacity. The engineering specifications used in estimating costs are summarized in Table 24 and the capital and annual costs are given in Table 25.

At over $5.00 per tonne of P_2O_5 product, the control cost for this system of scrubbers is very high in both sizes of plant. Approximately one third of the cost is attributable to control of fluoride emissions from storage buildings. The cost here is particularly high because of the large volume of air that must be scrubbed.

Some information has been supplied on the control of fluoride emissions from a conventional superphosphate plant in which the gases from the den are scrubbed in a two-stage scrubber system. Fluoride emission rates of less than 0.04 kg/tonne of product are achieved when single superphosphate is made, and less than 0.01 kg/tonne when triple superphosphate is made. The scrubber system and 50 m stack has a replacement value of £50 000 ($125 000). The gas flow is 20 000 m^3/h for a production rate

TABLE 23. - Capital and Annual Costs for Spray Cross-Flow Packed Scrubbers on Phosphoric Acid Plants

Plant Capacity tonne/d P_2O_5	450		800	
Gas Flow, m^3/h (16°C)	Typical Flow 110 000	Reduced Flow 37 000	Typical Flow 160 000	Reduced Flow 53 000
Capital Cost, $				
Scrubber	32 000	15 000	40 000	19 000
Auxiliary Equipment (fan, pumps etc.)	18 000	11 000	20 000	12 000
Installation	42 000	34 000	50 000	39 000
Total	92 000	60 000	110 000	70 000
Annual Cost, $/y				
Operating Labour	2 000	2 000	2 000	2 000
Maintenance (5%)	4 600	3 000	5 500	3 500
Utilities	7 300	2 500	10 600	3 500
Depreciation (10y)	9 200	6 000	11 000	7 000
Interest (8%)	7 360	4 800	8 800	5 600
Taxes and Insurance (2%)	1 840	1 200	2 200	1 400
Administration (5%)	4 600	3 000	5 500	3 500
Total Annual Cost	36 900	22,500	45 600	26 500
Cost per Tonne of P_2O_5*	$0.25	$0.15	$0.17	$0.10

*Assuming 330 days/y operation

TABLE 24. - Engineering Specifications for Estimating Air Pollution Control Costs for Granulated Triple Superphosphate Plants

Plant Capacity	230 tonne/d		360 tonne/d	
	Particulate Scrubber	Fluoride Scrubber	Particulate Scrubber	Fluoride Scrubber
A. Reactor-Granulator				
Gas to Scrubber, m^3/h at 60°C	43 500	39 000	70 000	62 000
Moisture Content %	11	7	11	7
B. Drier				
Gas to Scrubber, m^3/h at 82°C	94 000	-	149 000	-
Moisture Content %	12	-	12	-
C. Cooler and Transfer Points				
Gas to Scrubber, m^3/h at 60°C	99 000	-	159 000	-
Moisture Content, %	3	-	3	-
D. Storage				
Gas to Scrubber, m^3/h at 27°C	-	171 000	-	274 000
Moisture Content, %	-	2	-	2

TABLE 25. - Capital and Annual Control Costs for Granulated Triple Superphosphate Plants

Plant Capacity	230 tonne/d		360 tonne/d	
Costs in $	Particulate Scrubber	Fluoride Scrubber	Particulate Scrubber	Fluoride Scrubber
A. Reactor Granulator				
Capital	93 300*	43 700	130 000	60 700
Total Annual Cost	44 300	17 000	64 000	23 400
B. Drier				
Capital	179 000†	-	247 000	-
Total Annual Cost	106 500	-	157 000	-
C. Cooler and Transfer Points				
Capital	186 000†	-	259 000	-
Total Annual Cost	111 700	-	160 000	-
D. Storage				
Capital	-	335 000ϕ	-	465 000
Total Annual Cost	-	140 000	-	202 000
Total Capital, $	837 000		1 162 000	
Total Annual Cost, $/y	420 000		606 000	
Control Cost, $/tonne P_2O_5	5.53		5,10	

*Venturi - Cyclonic Scrubber

†Venturi - Packed Scrubber

ϕCyclonic Scrubber

Gypsum pond water used as scrubbing medium.

of 30 tonne/h (720 tonne/d). Details of the running costs of this plant are not available, but the total capital investment per tonne of capacity is about one twentieth of the costs in Table 25. The control cost in this plant is therefore probably not more than $0.50 per tonne of P_2O_5. This does not include any control of emissions from the storage building.

Fluorine Recovery

There are three possible sources of fluorine for conversion to useful by-products. The liquor from the reactor scrubber on a phosphoric acid or superphosphate plant will contain fluorosilicic acid. The vapours from the concentration unit on an acid plant can also be scrubbed to recover fluorosilicic acid. Alternatively sodium or potassium fluorosilicate can be precipitated from the 30% P_2O_5 filter acid.

The economics of fluorine recovery from the reactor vapours are not very favourable. The scrubber solution must be recirculated, and the maximum concentration of fluorosilicic acid that is produced is only about 10%. It is possible to recover approximately 2 kg of fluorine/tonne of P_2O_5 from air-cooled reactors. In systems using vacuum cooling about half the volatilized fluorides are absorbed in the barometric condenser water and are not recoverable. The potential for recovery is reduced to about 1 kg of fluorine/tonne of P_2O_5[53].

Commercial-scale processes have been used for the precipitation of sodium or potassium fluorosilicate from filter acid. There are several disadvantages to these processes. They do not work equally well on phosphoric acid made from all types of rock because the precipitation can be adversely affected by the presence of trace impurities. More than the theoretical amount of sodium ion must be added in order to obtain good yields and filterable crystals, so that if sodium carbonate is used to precipitate the fluorosilicate some of the phosphoric acid will be neutralized. On the other hand, if sodium chloride is used, the presence of chloride ion increases corrosion problems in the subsequent concentration of the phosphoric acid.

The most attractive source of by-product fluorides is the vapour from the concentration of 30% P_2O_5 acid. A phosphate rock containing 4% fluorine is theoretically capable of yielding 140-150 kg of fluorosilicic acid/tonne of P_2O_5. Assuming 40% of the fluorine is liberated in the concentration unit and an efficiency of 80% in the fluorine recovery unit a yield of 40-45 kg of fluorosilicic acid/tonne of P_2O_5 is possible.

Two commercial processes have been patented for use with a vacuum evaporation system[67]. The Swenson system condenses the vapours from the evaporator in a weak fluorosilicic acid solution. The liquor passes to a flash vessel at a lower pressure where an amount of water evaporates, equivalent to that originally condensed. This vapour then passes to a condenser. The liquor is cooled by the evaporation and recirculated to the first scrubber. A small amount of liquor is bled off as 15% fluorosilicic acid solution, and fresh water is added to the recycle solution as make-up.

The Swift system is simpler in operation and appears to be the more popular of the two. Vapours from the flash chamber of a phosphoric acid evaporation plant are scrubbed with fluorosilicic acid solution in a void spray tower. The acid is at the same temperature as the vapours and so essentially no condensation takes place. The vapours from the scrubber pass through an entrainment separator to remove droplets and then to the usual total condenser. Fluorosilicic acid at 18-20% concentration is bled off and water is added as make-up.

Uses for Fluorosilicic Acid and Fluorosilicates

At the present time the demand for fluorosilicates is quite small. Small quantities of by-product fluorosilicic acid and sodium fluorosilicate (which is sparingly soluble in water) are used in the ceramic industry, for the fluoridation of domestic water supplies and in toothpaste. There is still considerable controversy about the safety and wisdom of fluoridation[68]. The Health Departments of France and Italy have never accepted fluoridation as a safe procedure. It is illegal in Denmark. There have been trials in Germany and Belgium, but the Governments of these countries are against any further extension of the method. The Health Department in Holland strongly promotes fluoridation, but the State Council only gives permission where an alternative source of unfluoridated water is available. In Britain the decision lies with local authorities, so that the method has only been partially adopted.

The market for fluorosilicic acid is therefore very limited. Recovered fluorine from a 70,000 tonne/y phosphoric acid plant could be used to manufacture 3500 tonne/y of sodium fluorosilicate. The capital investment for a sodium fluorosilicate plant of this size would be £300,000 and a return on investment of 8% could be expected. The output from one plant, however, would be more than sufficient to satisfy the demands of the UK market. For these reasons, as well as the technical problems already mentioned, ICI have closed their plant for precipitation of sodium fluorosilicate.

In the UK Fisons recover fluorosilicic acid from recycled scrubber liquors from two out of three single superphosphate plants, and a Swift type unit is under construction on one of their phosphoric acid plants. The running costs of this unit are not yet known, but they are expected to depend upon the effect of the fluorine stripper on the operation of the phosphoric acid evaporator. The capital cost is high, amounting to about two thirds of the original cost of the evaporator. The amount of fluorine recovery in other countries is also very small. There is, however, an increasing demand for fluorine compounds in industry, and with this in mind a number of processes have been developed for the manufacture of saleable products from fluorosilicic acid[69].

Calcium fluoride, or fluorspar, is used in the steel industry and to a lesser extent in the ceramic industry. It is also used for the manufacture of several important fluorine compounds. It is an essential raw material for the manufacture of aluminium fluoride (AlF_3) and synthetic cryolite (Na_3AlF_6) which are used in the production of aluminium. Another important use is in the manufacture of fluorocarbons (via hydrofluoric acid) for the preparation of aerosols, refrigerants and polymers. Although world consumption of fluorspar only rose by 2% from 4.5 million tonnes in 1971 to 4.6 million tonnes in 1972, growth in consumption during the period 1966-1971 had averaged nearly 10% per annum[70]. This rate of increase has caused some concern about the adequacy of supplies of naturally occurring fluorspar. It seems possible, therefore, that there will be an increasing demand for fluorosilicic acid in the future, although there are new processes on the horizon in the aluminium and steel industries which do not require the use of fluorides. The demand for fluorosilicic acid in the 1980's might therefore be less than would be predicted from present trends.

The only process to have reached commercial scale in Europe was developed by Oesterreichische Stickstoff Werke. Aluminium fluoride is manufactured in a 5000 tonne/y plant at Linz by heating a dilute solution of fluorosilicic acid with aluminium hydroxide. Precipitated silica is filtered off and the aluminium fluoride is crystallized as the trihydrate.

Recently a Dutch process for the continuous production of aluminium fluoride was announced[71]. Ammonia and fluorosilicic acid react to form ammonium fluoride and silica. After the silica has been removed, excessive phosphate impurities are precipitated. The next stage is the reaction of ammonium fluoride with Gibbsite ($Al_2O_3.3H_2O$) to form a mixture of ammonium cryolite and alumina which is dried and calcined. Finally the ammonia is recovered and recycled. The process is at present at the pilot-plant stage. It is claimed that the present potential world output of 500 000 tonnes of fluorosilicic acid from the fertilizer industry should be sufficient to satisfy the aluminium industry, for which the process was specifically designed. The estimated production cost of aluminium fluoride by this process is £44.46/tonne, not including capital charges. By-product fluorosilicic acid from the production of 1600 tonnes/d of phosphoric acid could produce 100 tonnes/d of AlF_3. The investment for an AlF_3 plant of this size would be about £320 000[72].

Of the other processes which have been proposed for the use of waste fluorosilicic acid, two routes devised on the laboratory scale by the US Bureau of Mines are of particular interest because of the thorough economic analysis which has been published[73]. The first process involves conversion to fluorspar by precipitating the silica with ammonia followed by reaction of the filtrate with calcium hydroxide. In the second process lime, silica and fluorosilicic acid are reacted at a pH of 9.0-9.5 to precipitate both calcium fluoride and silica. The combined precipitate is pelleted and fed to a kiln, where, at a temperature in excess of 1000°C and in the presence of water, hydrofluoric acid is produced by pyrohydrolysis. The lowest estimated product sales prices required to yield a 25% return on investment (on a discounted cash flow basis) was $339.34/(short) ton of hydrogen fluoride and $48.64/ton of calcium fluoride. Compared with 1970 prices these calculations indicated that the processes considered could be profitable.

Disposal and Use of By-product Gypsum

In the manufacture of phosphoric acid 4.4-5.3 tonnes of gypsum are produced per tonne of P_2O_5, according to the P_2O_5 content of the phosphate rock[39]. The gypsum is separated by filtration and the filter cake contains approximately 25% free water. It has been estimated that 10 million tonnes of by-product gypsum were produced in Western Europe in 1971[74], so that, at least in some places, a serious disposal problem exists.

A few years ago a survey of 18 major phosphoric acid plants using dihydrate processes with a total annual capacity of over 1 million tonnes of P_2O_5 was carried out[75]. The methods of disposal used were:

10 plants - disposal into the sea or estuaries
2 plants - disposal into tidal rivers
3 plants - dumping on land
2 plants - dumping in excavated areas and old mines
1 plant - gypsum settling pond

The most satisfactory method of disposal, whenever it is possible, is generally regarded to be disposal by pipeline into sea water. This is the practice at all but one site in the UK. After removal from the filter the gypsum is slurried with about a tenfold quantity of water (often seawater) and pumped into the sea. The solubility of gypsum in sea water is higher than in fresh water (3.5 g/l in sea water compared with 2.3 g/l in fresh water). Nevertheless, in order to obtain rapid dissolution in the sea water the end of the pipeline should be located in such a way that the gypsum is well dispersed. At Leith in Scotland it was found that the gypsum dissolved within about 18 m of the point of discharge and the acidity of the effluent was removed by dilution in the same distance[76] (the effluent from the fluoride scrubbers is often used to slurry the gypsum). Small amounts of unreacted phosphate rock and fluorosilicates were deposited, but no increase in sulphate levels in the nearby dock have been recorded.

When the plant is located on a tidal river the situation is more difficult. At a plant in Belgium gypsum is only discharged on the ebb tide to ensure complete dispersal. The Windmill fertilizer works in Holland is about 20 km from the coast, so that it is necessary to transport the gypsum to the sea by barge. In most countries gypsum disposal into inland rivers is not allowed.

By-product gypsum contains about 96% calcium sulphate dihydrate, 1.5% unreacted phosphate rock, 0.2% soluble phosphate, 1% insoluble fluorosilicates, together with compounds of iron, aluminium and other metals and some organic compounds. In addition there will be additional water-soluble fluorine if scrubber water is used to slurry the gypsum. These materials will all add to the pollution load of the effluent stream.

In at least two plants in Germany the dry filter cake is carried by truck to mines or excavated areas and dumped. At other locations it is dumped on land, where land is available for this purpose. At Billingham in the UK gypsum is dumped on low-lying land, landscaped and then covered with top-soil on which barley has been successfully grown. It should be possible to use the land for future industrial development, though sulphate-resistant concrete would have to be used. It is claimed that this causes no environmental damage because there is no water movement through the gypsum and no evidence of leaching of fluoride or trace elements. Occasionally by-product gypsum has been used for land reclamation schemes, particularly when the land has been previously flooded with sea water.

The use of gypsum settling ponds is much rarer in Europe than it is in the United States. When this done it is the usual practice to recirculate the water from the pond for cooling and fluoride scrubbing. As the water is recycled dissolved impurities will build up until an equilibrium concentration is reached. Soluble fluoride concentrations of 3000-5000 mg/l are typical, and this gives rise to a significant partial pressure of fluorides in the atmosphere. On windy days up to 90 kg of fluorine can be lost to the atmosphere, though the concentration in the atmosphere will be very low.

Comparative costs for gypsum disposal by pipeline, dry dumping and by barge have been published[76].

	Capital Cost,	Annual Operating Cost not including return on capital,
	£	£
pipeline	60 000	8 930
dry dumping	9 500	25 100
barging	77 500	34 850

These costs are only of relative significance, because they are several years old and only refer to one specific location. Factors such as the length of the pipeline versus the distance of transport via truck or barge would obviously come into any relative appraisal of these three disposal methods. They do indicate, however, that disposal by barge is considerably more expensive than disposal by pipeline or dry dumping. Some up to date disposal costs are:

Slurrying and pumping by pipeline	:	£1.50/tonne P_2O_5 produced
Carriage and dumping	:	£2.15/tonne P_2O_5 produced

As alternatives to disposal a number of processes which can use by-product gypsum have been proposed.

Ammonium Sulphate

The Merseburg process makes ammonium sulphate by the reaction between gypsum and ammonium carbonate. The process is operated in India using phosphatic gypsum. The limitation is the falling market for ammonium sulphate, which can now be met by by-product material from several sources, including some nitrophosphate processes, steel making and caprolactam manufacture. ICI has ceased production of ammonium sulphate by this process for this reason.

Cement-Sulphuric Acid

Gypsum is calcined to anhydrous calcium sulphate which is then blended with coke, clay and sand or shale and roasted to give cement clinker and sulphur dioxide. The latter is used for the manufacture of sulphuric acid. There are, however, numerous obstacles to the use of by-product gypsum. Fluorine must be removed to prevent damage to the catalyst in the contact plant, and the presence of P_20_5 in the cement would retard its setting time and reduce its strength. The process is very expensive to operate, and at present sulphur prices it is not attractive in Europe. Only one plant in the world has been built to use exclusively by-product gypsum, and that is in South Africa.

Lime-Sulphuric Acid

A process which uses carbon monoxide to reduce calcium sulphate to sulphur dioxide and lime has been developed[77]. It is claimed that the process is more economical to operate than the cement-sulphuric acid process, but it has not achieved commercial exploitation.

Plaster and Plaster Board

The most widely adopted process using by-product gypsum has been partial dehydration to hemihydrate for use in the manufacture of plaster building products. The impurities in the gypsum would affect the setting properties of the plaster and must be removed. Various purification techniques have been evolved based upon removal of impurities by washing or neutralizing the acid. ICI developed a process for the manufacture of plasterboard but production has now ceased. The process was discontinued for several reasons:

(i) The value of the product is very low because it is in competition with plaster from cheap natural gypsum or anhydrite.

(ii) Trace elements, which affect setting properties must be removed.

(iii) Choice of rock for the phosphoric acid process is dictated by the gypsum process.

In Germany, Gebr. Guilini GmbH have developed a process which is gaining acceptance[74]. By-product gypsum is washed with water, combined with additives, and treated with steam in a reactor to convert it to the hemihydrate form. It is claimed that the alpha form of hemihydrate is obtained which has superior properties. Cast gypsum panels are preferred to plasterboard in Germany and can be made directly without drying the product. A 120 tonne/d plant has been running since 1965 and a 200 tonne/d plant was scheduled to start production in August 1973. The cost of the 200 tonne/d unit is stated to be DM 10 million[78]. A licence has also been granted to an Irish company which intends to manufacture saleable products from its waste gypsum.

An alternative approach is to incorporate a calcium sulphate recrystallization step in the phosphoric acid process so that HPO_4^{2-} ions incorporated in the initial calcium sulphate lattice are released. In this way P_2O_5 losses in the process are reduced, and a by-product gypsum which is sufficiently pure for the manufacture of plaster is produced. This approach has received much attention in Japan, where natural gypsum is not available. One process of this type, developed jointly by Prayon and Central Glass of Japan, has been adopted in Europe. Plants using the Central Prayon process have been built in Belgium and Sweden. Calcium sulphate is obtained containing less than 0.2% P_2O_5, which can be rendered totally insoluble by neutralization with a base. The product contains less than 5% free water and is sufficiently dry for most applications. By-product gypsum for plasterboard is sold in Belgium at the rate of 600-1000 tonnes/d in competition with natural gypsum.

Trace Elements

Some phosphate rocks contain traces of highly toxic elements which may be of potential pollution concern. These include:

As, Cd, Cr, Hg, U.

These elements can appear in the fertilizer product and in the by-product gypsum. For example, up to 36 ppm of cadmium have been found in phosphate fertilizers[79]. One case is known in which a phosphoric acid producer had to apply for a special licence to discharge radioactive effluents into an estuary because of the presence of uranium in the phosphate rock[75]. Most of the uranium passes into the acid, but radium, a decay product is retained in the gypsum. Gypsum derived from phosphoric acid plants using sedimentary ores may have a relatively high level of radioactivity (i.e. a radium concentration of up to 25 pico-Curies/g), and this must be taken into account if by-product gypsum is used as a building material. The problem has been investigated in the UK by the National Radiological Protection Board[80]. It was concluded that if, after a few decades, by-product gypsum was used in, say, 10% of all buildings, the increase in the average population dose would be about 2% of the background dose observed over most of the country. The variation observed in background dose in different parts of the country is about ten times as great as this. It was decided that the material could be safely used provided that concentrations of radium in excess of 25 pico-Curies/g are avoided and arrangements are made for recording the production of the material and measuring its radioactivity.

Summary

There are two major pollution problems in the manufacture of phosphoric acid and superphosphates. One of these is the release of fluorides when phosphate rock is attacked by acid, and in the concentration of phosphoric acid from 30% P_2O_5 to as high as 54% P_2O_5. The other, not encountered in superphosphate manufacture, is the disposal of the vast quantities of by-product gypsum which are produced in phosphoric acid manufacture.

Fluorine losses of around 5 kg/tonne of P_2O_5 produced are possible in the digestion of phosphate rock, and between 20 and 60 kg of fluorine/tonne of P_2O_5 may be released in the concentration of 30% P_2O_5 acid. Atmospheric pollution can be controlled economically by simple wet scrubbers, so that less than 0.01 kg of fluorine/tonne of P_2O_5 is discharged to the atmosphere at a concentration of less than 50 mg/m^3. At the present time much of this fluorine is discharged with the aqueous effluent from the plant. Recovery of fluorine is technologically possible, and may become economically attractive as other traditional sources of fluorine become depleted.

Several processes have been developed for the use of by-product gypsum, but none of these is particularly economical in competition with cheap naturally occurring gypsum or anhydrite. Limited quantities of by-product gypsum are used in the manufacture of building materials, mainly in Germany.

AMMONIUM NITRATE

Process Description

Commercial processes fall into two classes. In those countries where 'nitrophosphate' fertilizers are made by the attack of nitric acid on phosphate rock, ammonium nitrate or calcium ammonium nitrate may be produced as a by-product. Ammonium nitrate is also manufactured directly by neutralizing nitric acid with ammonia, and this process is discussed here.

Anhydrous gaseous ammonia and nitric acid (usually 55-60%) can be neutralized in a vacuum, atmospheric or pressure neutralizer. The reaction is exothermic and the heat of reaction is sufficient to concentrate the neutralized solution to 82-87%:

$$NH_3 + NHO_3 \rightarrow NH_4NO_3$$

$$\Delta H \approx -26.7 \text{ kcal}$$

Prilling is the most common method of producing solid ammonium nitrate. A concentrated melt of ammonium nitrate is sprayed down a tower countercurrent to a stream of air which cools and solidifies the droplets. The solution from the neutralizer must be concentrated by evaporation before prilling. If the solution is concentrated to 95-96% the prills must be dried to reduce the moisture content to less than 0.5%. Alternatively the solution may be concentrated to greater than 99.5%. In this way high-density prills containing less than 0.2% moisture can be produced, eliminating the need for a dryer. This would probably be the preferred choice for a new plant. In order to minimize caking of the product due to moisture absorption the cooled prills are coated with clay or kieselguhr. Alternatively an internal desiccator can be added to the ammonium nitrate before prilling[81]. A simplified flow-sheet for a typical ammonium nitrate process is shown in Fig. 8.

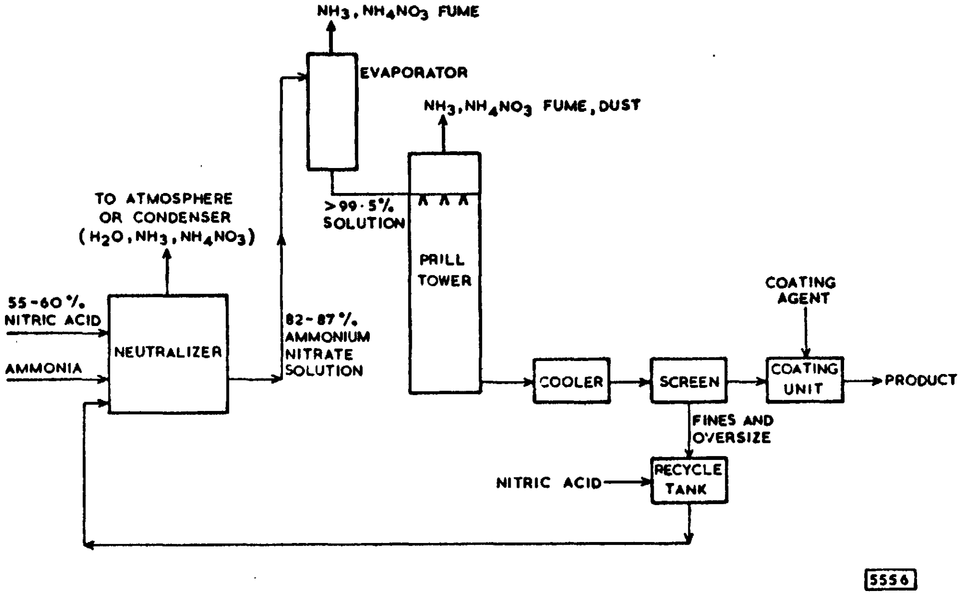

FIG.8 FLOW SHEET FOR AMMONIUM NITRATE PRODUCTION

In the Stengel process ammonia and nitric acid are mixed under pressure. The process produces a high-concentration melt which is not prilled, but solidified by a cooled stainless steel belt and discharged as solid flakes which are broken up mechanically.

Ammonium nitrate may also be granulated, or mixed with powdered limestone to produce lime ammonium nitrate, a lower-grade fertilizer.

Sources of Pollution

There are four main sources of discharge to the atmosphere of gases containing small quantities of ammonia or ammonium nitrate. They are the neutralizer, the evaporator, the prilling tower and the cooler. If one is installed, the dryer is an additional source. The greatest losses occur in the neutralizer. Atmospheric pollution from this source is often avoided by condensing the large quantities of steam produced in the reaction, but at the expense of creating an aqueous effluent problem. The prilling tower cooler and drier are sources of ammonium nitrate dust, which settles close to the plant and adds to the water pollution load of the plant in storm water run-off.

The dangers of combustion and explosion when ammonium nitrate is handled are well known, and this gives rise to considerable problems in designing an ammonium nitrate plant. The conditions which are least hazardous are often not those which minimize pollution, and some compromise must be reached. Combustion of ammonium nitrate is catalyzed by the presence of chloride, organic materials and some metals[81,82]. It is therefore dangerous to recycle spilled material to the process, although it may be processed in a compound fertilizer plant, where it does not pass through an evaporator and is diluted with other material. The principles of the design of an ammonium nitrate plant taking into account the dual requirements of safety and effluent control have been described by Carter and Roberts[81]. Much of the following discussion is based upon the type of plant described in their paper. While other designs may differ in detail, the principles discussed should be generally applicable.

The Neutralizer

The nitrogen loss in the neutralizer depends upon a number of factors. Ammonium nitrate losses due to the carry-over of entrained droplets of solution can be minimized by careful vessel design. This also applies to ammonia losses due to incomplete reaction with nitric acid. There is, however, another source of ammonia losses which is more difficult to control, which is the equilibrium vapour pressure of ammonia over the surface of the liquid in the neutralizer.

The ammonia vapour pressure increases with pH and therefore the loss of ammonia can be reduced by lowering the pH. This increases the hazards involved in handling the liquor, however, and the technique has therefore evolved of carrying out the neutralization in two stages. In the first stage, the relatively low pH reduces the ammonia loss, although the rate of steam evolution is high. In the second stage the pH is increased by adding a small amount of ammonia. The vapour pressure is higher but steam evolution is negligible. The combined loss from the two stages may be a factor of 5 to 10 times less than that of a single neutralization operating at a pH equal to that in the second stage. Careful pH control is necessary to achieve satisfactory operation of such a system[81].

Nitrogen efficiencies of greater than 99% are possible. If the steam evolved in the neutralizer is condensed atmospheric pollution is negligible, e.g. less than 1 tonne/y for a 500 tonne/d plant[81]. The condensate will, however, create a possible water pollution problem. Its composition will vary from process to process but some quoted values are given in Table 26.

TABLE 26. - Composition of Ammonium Nitrate Process Condensate

pH	ammonia,%	ammonium nitrate,%	Reference
<7	0.1	0.6	82
two stage (1) <7 (2) >7	up to 0.5	negligible	81
5	-	1.5 - 2.5 (up to 12% in upset conditions)	83
not specified	∿1	0.2 - 0.3	84
"	<0.1	<0.2	84
"	0.9	0.3	84

Losses in the condensate are minimized if the reactants are supplied to the neutralizer in stoichiometric proportions. A control system to achieve this has been described[85]. It was shown that in-plant control was successful in reducing the aqueous effluent from the plant.

The Evaporator

In a plant producing high density prills it is desirable for safety reasons that pumping of the concentrated ammonium nitrate melt should be avoided. This can be done by placing the evaporator at the top of the prilling tower, in which case the evaporator and prilling tower effluent will effectively come from the same source. Losses from the evaporator will include ammonia stripped off in the air stream, ammonium nitrate fume and carry-over of liquid droplets. The evaporator in a typical 500 tonne/d plant emits 8000 m^3/h of air/water vapour at 160°C containing 500 mg/m^3 ammonium nitrate. This amounts to a loss of 0.2 kg/tonne of product. Ammonia losses can be reduced by careful control of pH in the secondary neutralizer. Ammonium nitrate fume can be minimized by careful design of the equipment and is treated in greater detail below. Carry-over of liquid droplets can be controlled by fitting a suitable demister. An effluent condenser can be used to eliminate the steam plume if required.

The Prilling Tower

There are three contributions to the effluent from the prilling tower:

Carry-over of prills (i.e. ammonium nitrate dust)
ammonium nitrate fume
ammonia.

Prill Carry-Over

Droplets of ammonium nitrate melt can be formed in a variety of ways, e.g. from a rotating bucket or by slow discharge through an orifice. The dust problem from a prilling tower arises because of the formation of a wide range of sizes of droplets.

The size range which is aimed for in the product is usually about 1-3 mm. When the droplets are formed from the break up of a jet of the melt formed by an orifice, small satellite droplets are formed in addition to the droplets within the desired size range. These form micro-prills, and if the free-fall velocity of the micro-prill is smaller than the velocity of air moving up the tower it will be carried out of the tower. The results of calculations of the total amount of carry-over for a 500 tonne/d plant are given in Table 27.

TABLE 27. - Carry-over of Micro-prills

Air Velocity, m/s	Maximum size of particles carried over, mm	Total carry-over, tonne/y
1	0.190	25
3	0.515	350

A factor of 3 in the air velocity produces a factor of 14 in the effluent produced. If the calculation is carried out in terms of the rate of deposition of dust on the ground it is found that the maximum rate of deposition is increased by a factor of 180 for the same increase in air velocity[81]. Bearing in mind that air velocities as high as 5 m/s are used in some designs, the amount of effluent dust can be considerable. At one plant which has been visited, particles less than 0.3 mm are carried over at a rate of up to 50 kg/h, which amounts to 0.2% of production. This figure is well above the minimum of 0.05% of production at a concentration of 50 mg/m^3 which has been quoted to the author and which should be achievable in a well-designed plant.

The dust emitted from a prilling tower is deposited on the ground close to the tower and is therefore only likely to be a nuisance on or very near to the factory site. It will, of course, dissolve in rain water and form part of the aqueous effluent from the plant. At less than 0.2% of production it will however make a smaller contribution to the total aqueous effluent than process leaks and spills.

Ammonia and Ammonium Nitrate Fume

Ammonium nitrate fume consists of small solid particles, generally less than 5×10^{-3} mm in size, formed by evaporation and subsequent condensation or by chemical decomposition and subsequent recombination in the air. It can appear as a dense blue smoke[86], but in a well-designed plant it should be no more than a faint bluish haze.

The evolution of both ammonia and fume depends upon melt pH, melt temperature and the air velocity over the surface of the melt. The effect of pH is the same as that discussed in relation to neutralizers. It is possible to calculate an optimum pH at which the total loss in terms of nitrogen is minimized[81]. This turns out to be about 6.5, but there is a tendency to operate at a higher pH to give a less visible plume at the expense of ammonia losses which are higher than necessary. In industrial areas where there are appreciable amounts of sulphur dioxide in the atmosphere the ammonia may be more serious than is apparent because of the tendency to form ammonium sulphate with its attendant risk of mist formation.

The temperature frequently employed is 180-185°C, but it is possible to reduce the temperature slightly below this level, with a resultant reduction of effluent by a factor of about two. The effluent can also be reduced by reducing the velocity past the surface of the liquid droplets. This can be done by withdrawing some air at a point below the spray roses. Finally the overall effluent problem is affected by the mechanical design at the top of the tower.

By careful design of the equipment, taking into account the principles discussed, and with the use of accurate control systems it should be possible to reduce the losses due to ammonia and ammonium nitrate fume to less than 0.05% of production. At this level the fume is not persistent and disperses quickly. There are, however, very few plants in existence which are capable of achieving such low effluent levels. The amount of atmospheric pollution from most plants is probably at least ten times higher.

Coolers and Driers

Air streams from coolers and driers can contain large quantities of ammonium nitrate dust. Because of the relatively small quantity of air to be treated wet scrubbers can be used to recover the ammonium nitrate and return it to the neutralizer. The scrubbing medium is a solution of ammonium nitrate. Recovery in this way is economical and there should be no air pollution problem from this source.

Granulation Plants

Granulation plants produce similar effluents except that air from granulator, dryer and cooler replaces that from a prilling tower. For a 500 tonne/d plant approximately 120,000 m^3/h of air would be involved and dust burdens can typically be 200-500 mg/m^3 depending on degree of cyclone separation/wet scrubbing employed.

Control Techniques

Most processes have no control on the prilling tower exhaust. It would be possible to scrub the larger particles from the effluent, but it is a difficult problem because of the vast quantities of air involved and the low pressure drop available for scrubbing equipment. The combined capital cost of the scrubber and extra running cost of the fans due to the increased pressure drop required is frequently higher than the cost of additional tower height necessary to decrease the air velocity sufficiently to cause an equivalent reduction in the effluent. In addition wet scrubbing would not have much effect on ammonium nitrate fume, and would tend to produce a wet steamy plume in cold weather.

Dust deposition from a prilling tower can be kept to low levels by using a low air velocity in the tower. When the tower is fully loaded the carry-over of dust must be balanced against the degree of cooling required to solidify the prills. If the tower is only lightly loaded it will be possible to decrease the air velocity. At one plant in the UK the prilling tower is used for compound fertilizers as well as straight ammonium nitrate. When ammonium nitrate is produced only two of the prilling tower's four fans may be required. The amount of carry-over under these conditions is so small as to be unmeasurable, and the only effluent from the tower is ammonium nitrate fume.

It is clear from the preceding sections that it is possible to design an ammonium nitrate plant to give very low effluent levels. The losses to the atmosphere from the prilling tower can be kept down to about 0.1%. Most of the nitrogen loss in the process occurs in the neutralizer and is less than 1%. Pollution control to these standards requires high capital investment amounting to 25% of the capital cost of the plant, i.e. an increase of £250 000 for a 1200 tonne/d plant. This is equivalent to an increase of $0.56/tonne in production cost.

If the steam effluent from the neutralizer is condensed this gives rise to an aqueous effluent problem, because this solution is much too dilute to recycle to the neutralizer. In some plants the condensate is partially recycled to the absorption tower of the nitric acid plant, but other operators regard the procedure as hazardous. The problem is the possible formation of ammonium nitrate and nitrite in the absorption tower and energy recovery equipment. However, tests have been carried out which showed that recycling of the condensate should be quite safe provided that its pH is carefully controlled[83]. It is important to ensure that no free ammonia enters the absorption tower of the nitric acid plant. In one plant where condensate is recycled its pH is controlled at less than 2 by addition of acid. If this pH is exceeded the condensate is automatically dumped to drain.

Even when the process condensate is recycled to the nitric acid plant it is not possible to dispose of it completely in this way. Consider the production of 87% ammonium nitrate from 60% nitric acid. The process will require 0.8 tonnes of nitric acid per tonne of ammonium nitrate. In the neutralizer 375 kg of steam will be produced per tonne of ammonium nitrate product. Because the production of 0.8 tonnes of nitric acid at a concentration of 60% only requires 288 kg of water in the absorption tower there is an excess of 87 kg. There may be additional excess water if the process involves incorporation of additives in aqueous solution, or if steam from the final concentration of ammonium nitrate to 99.5% is condensed. Specifications for two processes, for example, indicate the formation of 500-600 kg of steam in the neutralizer per tonne of ammonium nitrate. It is therefore only possible to use 50-75% of the condensate in the nitric acid plant.

A two stage scrubbing system for purification of the steam from the neutralizer has been described[87]. Applied to a 300 tonne/d plant this system recovers 14 kg of ammonium nitrate per tonne of product and permits discharge of the neutralizer vapours to the atmosphere.

Summary

The greatest losses in ammonium nitrate production occur in the neutralizer. Carry-over of entrained ammonium nitrate can be minimized by careful design but in order to reduce losses of ammonia it is necessary to use two stages of neutralization. The overall nitrogen loss can be kept to less than 1% of production. The condensate from the neutralizer can be used as process water in a nitric acid plant absorption tower provided that the pH is carefully controlled.

Emissions to the atmosphere from the prilling tower include ammonia, ammonium nitrate fume, and dust. Careful design of the tower can reduce these effluents to very low levels but the cost can be as high as 25% of the capital cost of the plant.

AMMONIUM SULPHATE

With the trend towards higher analysis fertilizers since the mid-1960's, there has been a tendency in many countries for the use of ammonium sulphate to decline. In a survey published in 1972[88] it was predicted that the total increase in the ammonium sulphate market during the 1970's would amount to about 25%, which is very moderate compared with the growth in the 1960's. Also, synthetic material manufactured by the fertilizer industry is gradually being replaced by material indirectly produced by other industries. Of increasing importance is ammonium sulphate derived as a co-product in caprolactam manufacture and, to a lesser extent, from the production of acrylonitrile and other artificial fibre intermediates. Some of the older caprolactam processes produce as much as 4.6 tonnes of ammonium sulphate per tonne of caprolactam, and the limited market has led to the development of newer processes which reduce or even eliminate completely the quantity of ammonium sulphate produced[89]. By-product material from coke ovens and steel works also comprises a major source of ammonium sulphate, and increasing quantities may become available as a product of processes for the abatement of sulphur dioxide pollution.

These developments have naturally led to a decline in the manufacture of synthetic ammonium sulphate by the fertilizer industry. Table 28 shows the sources of ammonium sulphate in 1969/70 in the countries which now form the EEC.

TABLE 28. - Production of Ammonium Sulphate 1969/70

(1 000 Tonnes N)

Country	Synthetic	Coke-oven	Co-product
Belgium/Luxembourg	-	7.0	85.7
France	30.2	15.0	-
Germany	56.3	81.0	50.0
Ireland	29.0	-	-
Italy	175.8	13.0	50.0
Netherlands	-	-	109.8
UK	60.0	46.4	52.0

By 1969 synthetic ammonium sulphate production had completely ceased in Belgium and the Netherlands. This now also applies to the UK, ICI having closed down its plant for the production of ammonium sulphate from anhydrite in 1971. Similarly in France there is now only one plant producing synthetic ammonium sulphate and most of the country's output comes from the textile industry. Italy is the major exception to the general trend, though with increasing caprolactam capacity coming into operation this situation may soon change. Output of synthetic material has also expanded in Ireland during the last decade.

In view of the declining importance of ammonium sulphate synthesis in the fertilizer industry, the processes used will not be described in any detail. It is sufficient to say that production is either by the reaction between ammonia and sulphuric acid in a crystallizer, or by the reaction between calcium sulphate and ammonium carbonate in the Merseburg process. In the former process there are the usual losses of reactants in the steam which is evolved during neutralization. Ammonia can be removed from the steam in a water scrubber, a barometric condenser or an indirect condenser. Where indirect condensation is used the condensate can be returned to the process. Otherwise an aqueous waste stream is generated which contains between 10 and 100 g/m^3 of ammonia and a similar concentration of sulphate when the water is used on a once-through basis[4]. If the water is recycled these concentrations will be much higher. The volume of water used can vary between 0.42 and 42 m^3/tonne of product, depending upon whether water is recirculated or not. In one European plant the ammonia concentration in the steam is kept below 10-15 ppm by control of free acid concentration in the crystallizer. The off-gas from the ammonium sulphate dryer contains ammonium sulphate particles and small amounts of ammonia. The particles can be collected in a dry cyclone and returned to the process. Ammonia can be recovered in a scrubber if necessary, giving rise to a low concentration solution, usually containing less than 10 g/m^3 of ammonia.

As is mentioned in the section on phosphoric acid, the Merseburg process has been proposed as a means of disposing of by-product gypsum, although it is not operated as such in Europe. It is, however, operated in Italy using natural calcium sulphate, and accounts for an annual production of over 500 000 tonnes of ammonium sulphate. As a solution to the gypsum problem, the process is obviously not regarded as a major source of pollution. Calcium carbonate is produced as a by-product, amounting to 0.75 tonnes/tonne of ammonium sulphate. This can be mixed with ammonium nitrate and sold as a fertilizer product.

In summary, the processes for the synthesis of ammonium sulphate used by the fertilizer industry have declined in importance and have disappeared completely in some countries. This trend is likely to continue as the quantities of ammonium sulphate produced in other industries increase sufficiently to meet the demand (which may remain at a significant level due to the existence of sulphur deficiencies in some crops). The contribution of ammonium sulphate to the pollution generated by the fertilizer industry is small and unlikely to increase.

AMMONIUM PHOSPHATES

Process Descriptions

Ammonium phosphate fertilizers are made by the ammoniation of wet process phosphoric acid. Until 1959 the extent of ammoniation was controlled to yield a slurry composition ranging from mono-ammonium phosphate (MAP) to about two thirds di-ammonium phosphate depending upon the grade of product desired. This was followed by the development of the TVA process for the manufacture of di-ammonium phosphate (DAP). This process has achieved great importance as one of the principal routes to granular NP and NPK fertilizers and will be described in the section on these products.

In recent years a powder or non-granular form of mono-ammonium phosphate has been produced and marketed as a fertilizer intermediate. The two processes which have achieved the widest application are rather different in operation. In the SAI process phosphoric acid is neutralized with ammonia at a $NH_3:H_3PO_4$ molar ratio of about 1:3. The resulting slurry is transferred to the 'moisture disengagement zone' where further phosphoric acid is added to reduce the molar ratio to 1.0. The resulting heat of reaction and low solubility of MAP give rapid evolution of moisture and solidification of product. In the 'Minifos' process neutralization at a molar ratio of 1.0 is carried out at 165-170°C in a pressure vessel. The resulting concentrated solution is sprayed into a short natural draught tower where a fine powder product is formed. Plants have been built in France, Holland, Italy and the UK, as well as other countries outside the EEC. The process is illustrated in Fig. 9.

Sources of Pollution

Ammonia losses in the neutralizer depend upon the molar ratio $NH_3:H_3PO_4$, and can

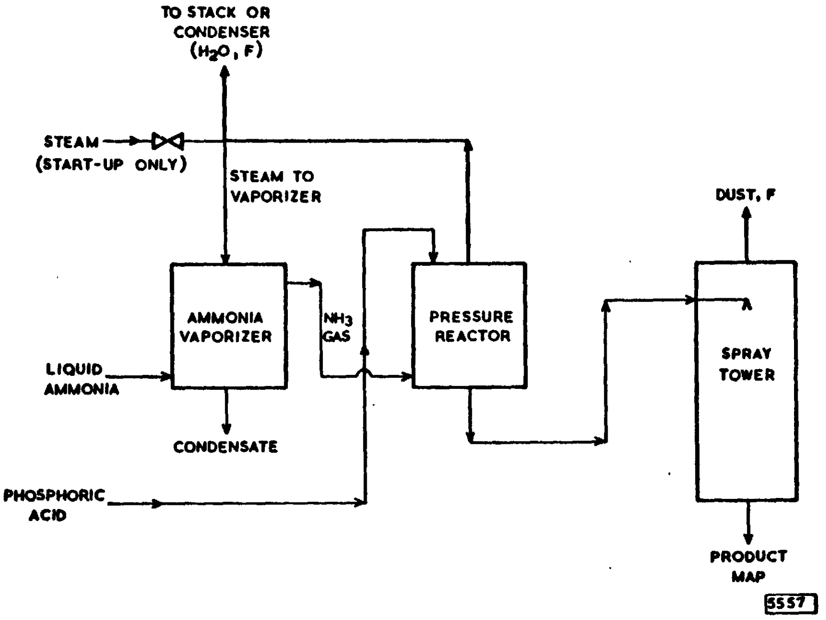

FIG. 9 FLOW SHEET FOR THE PRODUCTION OF MAP

be high when the molar ratio is greater than 1.0. In the SAI process, therefore, the vapours from the neutralizer are scrubbed with phosphoric acid. In this respect the process is similar to the TVA process for DAP production described later, and the effluents will be similar. Ammonia losses in the Minifos process are negligible and no scrubbing is necessary. The steam evolved in the neutralizer amounts to 22 kg/tonne of MAP, and contains about 100 ppm by volume of fluorine (85 mg/m^3) i.e. about 2 g of fluorine/tonne of product. Such low quantities of fluorine can be discharged to the atmosphere in Europe, but must be condensed in the USA. The spray tower emits 5000 m^3 of air/tonne of MAP. The fluorine content is negligible (∿1 ppm), but a simple scrubber is used to reduce the dust content of the air to 150 mg/m^3. There is therefore a loss of 0.75 kg of MAP dust/tonne of product, and this represents the major effluent from the process.

UREA

Process Description

Urea is produced by the reaction between ammonia and carbon dioxide at elevated temperature and pressure. The reaction takes place in two stages:

$$2NH_3 + CO_2 \rightleftharpoons NH_2\,COONH_4 \quad \dots\dots (1)$$

$$NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O \quad \dots\dots (2)$$

The formation of ammonium carbamate by Reaction (1) is exothermic and goes to completion under reaction conditions. The dehydration of ammonium carbamate by Reaction (2) is endothermic and goes to 40-70% completion depending upon the process conditions. Reaction pressures are in the range 135-360 atmospheres absolute and temperatures within the range 170-200°C.

The product stream from the reactor consists of a mixture of urea, ammonium carbamate, water, ammonia and carbon dioxide. The final stages of the process involve decomposition of the ammonium carbamate, recovery of the urea product and possible recycle of unreacted ammonia and carbon dioxide. The earlier processes were once-through processes in which no attempt at recycle was made. Conversion of ammonia was about 45%, the remainder being used in the production of other fertilizer intermediates. Later developments have proceeded through partial recycle processes, in which the overall conversion efficiency was increased to about 80%, to total recycle processes. Two stages of ammonium carbamate decomposition are carried out in total recycle processes, the second one being at atmospheric pressure. The most recent development has been the introduction of stripping processes in which the ammonium carbamate is decomposed at reaction pressure. This is done by reducing its partial pressure with an atmosphere of carbon dioxide (DSM) or ammonia (SNAM-Progetti).

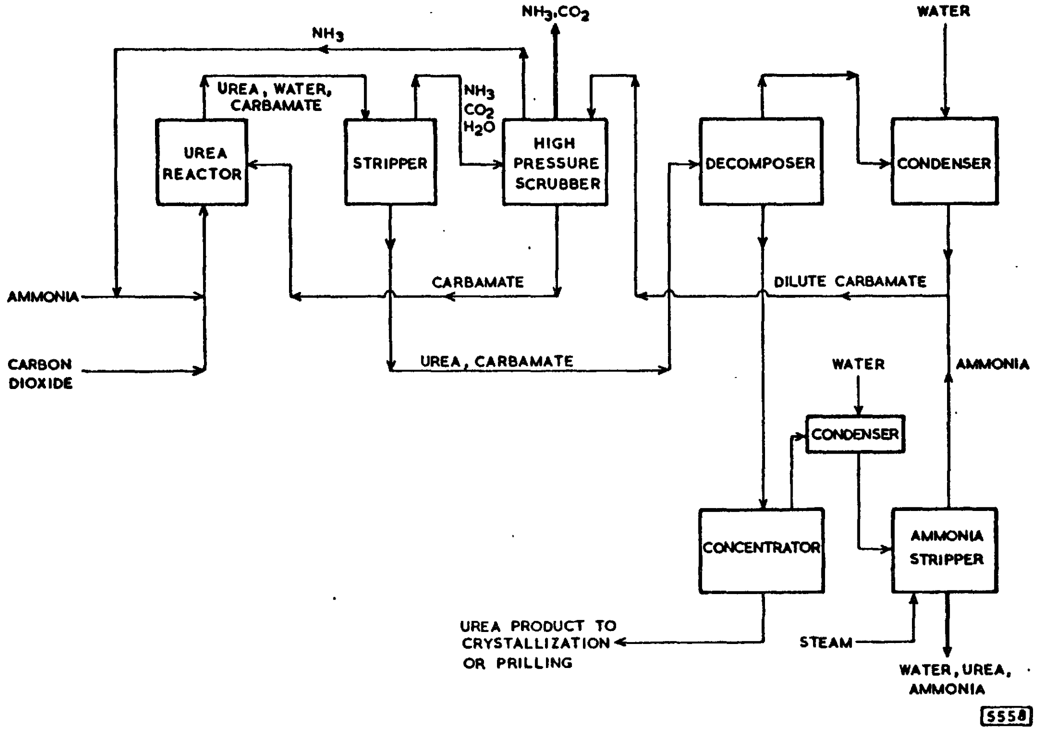

FIG. 10 FLOW SHEET FOR UREA PRODUCTION BY A TOTAL RECYCLE PROCESS

Figure 10 presents a simplified flowsheet of a typical total recycle urea process. The temperature in the reactor is about 185°C and the pressure 200 atmospheres. The reaction mixture flows to a stripping section where its pressure is reduced to about 20 atmospheres except in those new processes where carbon dioxide or ammonia are used for stripping. The gases from the stripper are washed to give a pure ammonia gas stream and an ammonium carbamate solution, both of which are recycled. The solution from the stripper flows to a decomposer where dehydration of the ammonium carbamate is completed at 5 atmospheres. Ammonia is stripped from the concentrator condensate with steam and returned to the process.

Urea synthesis by such a process produces a solution of 75-80% concentration. Vacuum evaporation followed by prilling yields a product containing around 1% biuret. If low biuret material is required (0.3%) an intermediate crystallization stage is necessary, followed by re-melting and prilling. Urea may also be produced as a crystalline product.

Sources of Pollution

There will be losses of ammonia and urea dust from the prilling tower. Similar considerations with respect to micro-prill formation and carry over of dust apply to urea as already discussed in the section on ammonium nitrate. In total recycle processes inert gases build up in the recycle system and must be purged. The purge stream will contain small amounts of ammonia and carbon dioxide and is normally discharged to the atmosphere. The urea solution from the decomposer will contain small amounts of ammonia and carbon dioxide. This ammonia will be evolved with the water vapour in the concentrator. Ammonia can also be released from the hydrolysis of urea in the concentrator. The condensate from this section of the plant gives rise to a considerable water pollution problem in urea manufacture. Ammonia losses as high as 2 kg/tonne of urea are possible, and the condensate will also contain significant quantities of urea.

Air Pollution

From the heat balance of the prilling tower 8000-10000 m^3 of air are required per tonne of prilled urea. The air outlet from the fans will contain ammonia and urea dust. Concentrations of 40 mg/m^3 of ammonia and 110 mg/m^3 of dust have been quoted in the vent gases from a 1000 tonne/d plant[90]. Dust loadings as high as 500-1000 mg/m^3 are quoted for a Japanese process[91] but here the air is ducted down to a simple scrubber in order to reduce the dust concentration to 80-100 mg/m^3. A crystallization plant will be fitted with dust cyclones but the concentration of urea dust at the cyclone outlet can be as high as 1250 mg/m^3 [90].

The outlet of the high pressure scrubber will release a mixture of steam and inert gases which were present in the carbon dioxide supply. This vent gas contains ammonia at a relatively high concentration (e.g. 7000 mg/m^3) because the total quantity of gas released is quite small.

The gaseous effluents from the carbon dioxide stripping process are summarized in Table 29. The figures for the concentrations and total quantities emitted per tonne of product probably represent minimum pollution levels achieveable in a modern plant.

TABLE 29. - Gaseous Effluents from a Urea Process

Source	Total m^3/tonne urea	Ammonia		Urea Dust		Carbon Dioxide
		mg/m^3	kg/tonne urea	mg/m^3	kg/tonne urea	kg/tonne urea
High Pressure Scrubber Vent	43	7000	0.32	-	-	15
Prilling Tower	10 000	40	0.48	110	1.3	-

Water Pollution

The concentrator condensate from the carbon dioxide stripping process contains minimum concentrations of 3000 g/m^3 of urea and 600 g/m^3 of ammonia[90]. The quantity of waste water discharged amounts to 0.5 m^3 per tonne of urea product. These concentrations can be considerably higher when the plant is not operating smoothly. Indeed, taken together with the losses to the atmosphere quoted in Table 29, the above figures imply an overall efficiency of 99.5% for the urea process. The opinion of the fertilizer industry is that such a high efficiency is unlikely to be achieved in practice.

In order to set this information for a particular process in perspective the composition of typical waste water streams from 14 urea plants in the USA[4] is shown in Table 30. These data are for the combined waste streams, including wash solutions from the cleaning up of process spills.

TABLE 30. - Waste Water Streams from Urea Plants in the USA

Contaminant	Concentration, g/m^3
Ammonia	200 - 4000
Urea	50 - 1000
Carbon Dioxide	100 - 1000
Oil	10 - 100
B O D	30 - 300
C O D	50 - 500

The volume of the waste streams in this survey varied between 0.2 and 8.4 m^3 per tonne of urea and could be very much higher than the 0.5 m^3/tonne of urea quoted for the carbon dioxide stripping process. This may be due to the use of direct condensers, which gives rise to large volumes of slightly contaminated waste water. The process condensate from urea plants is usually discharged to drain.

Control Techniques

It has already been mentioned in the section on ammonium nitrate that, because of the large quantity of air and the low pressure head of the fans, collection of the dust emitted by a prilling tower is very difficult. DSM have adapted a dust collector used for collecting coal dust for use on a urea prilling tower[90]. The dust-containing air impinges on guide vanes wetted by spray pipes, and dust particles are removed in the water for return to the process. The pressure drop across the guide vanes is only 3-5 mm W.G.* and the efficiency is expected to be 80%. The exit concentration of urea dust should therefore be reduced to about 20 mg/m^3. The investment required for such an installation was estimated to be $50 000, based on West-European conditions. The extra power cost is balanced by the value of the urea collected. The design of another scrubber for a urea prilling tower for which 98% efficiency is claimed has been described[91].

A simple dust collector to catch the dust from the cyclone exit of a urea crystallization plant has also been designed, based upon the impingement of urea dust on a liquid surface[90]. The pressure drop across the device is 40-50 mm W.G.* and the efficiency is about 75%. The urea is returned to the process as a 20% solution. The cost of this installation is about $16 000.

When direct condensers are used on the concentrator it will be difficult to recover ammonia by stripping because of the low concentration. One plant in Sweden[92] has recently been converted to indirect condensers in order to make it possible to strip the ammonia and return it to the process. DSM are developing a process which will reduce the urea concentration in the condensate to 200 g/m^3, and the ammonia concentration to 100 g/m^3 [90]. In the first stage the urea is hydrolyzed to ammonia at 180°C. The ammonia is then recovered by stripping with steam. In this way the ammonia and urea losses are reduced as shown in Table 31.

TABLE 31. - Urea Process Condensate after Hydrolysis and Stripping

	Composition of Aqueous Effluent per Tonne of Urea		
	Total, m^3	Ammonia, kg	Urea, kg
Without Treatment	0.5	0.29	1.44
After Hydrolysis and Stripping	0.5	0.05	0.10

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*1 mm W.G. = 9.81 N/m^2

In a 1000 tonne/d urea plant the total losses of ammoniacal nitrogen are reduced from 910 kg/d to 84 kg/d. In Holland the penalty imposed for the discharge of nitrogenous waste streams will shortly amount to Dfl 12 per population equivalent*. Application of the hydrolysis/steam stripping process would therefore reduce the annual penalty for discharge of the waste stream from Dfl 275 000 ($98 000) to Dfl 2600 ($9000). The extra capital investment for the equipment, including erection and engineering, was estimated in 1971 to be $125 000. Assuming the cost would now be $160 000, the economic aspects of the process are summarized in Table 32. It is clear that if a high penalty is applied to the discharge of the waste water it is more economical to invest in the extra equipment for purification of the waste stream.

TABLE 32. - Economic Data on the Operation of the Urea Hydrolysis/Steam Stripping Process

	Costs in $	
	without purification	with purification
Annual Penalty (in Holland)	98 000	9 000
Extra Steam Cost (at $1.90/tonne)	-	27 000
Investment Costs (at 30% per annum)	-	48 000
	98 000	84 000
Credit for Ammonia Recovery (at $50/tonne)	-	-14 000
Net Annual Cost	98 000	70 000

Further reduction in the nitrogen content of the waste stream is possible by biochemical oxidation. The process is described in the next section.

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*Population equivalent is defined in Appendix B.

TREATMENT OF WASTE WATERS FROM NITROGENOUS FERTILIZER PLANT

The waste water from nitrogenous fertilizer plants will contain nitrogen as ammonia (i.e. NH_4^+) and nitrate. There are several possible techniques for the removal from the effluent of nitrogen in these two forms. Ammonia can be removed by biological nitrification, ion exchange, and air or steam stripping. Nitrates can be treated by biological denitrification and ion exchange.

Biological Nitrification of Ammonia[93]

Biological nitrification is a process in which ammonia and some organic nitrogen compounds are converted to nitrates by two specific organisms, "Nitrosomonas" and "Nitrobacter". The reactions which take place are:

$$NH_4^+ + 1\tfrac{1}{2}\,O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + H_2O + 2H^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$NO_2^- + \tfrac{1}{2}\,O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The reactions occur under aerobic conditions and the bacteria obtain carbon from inorganic sources such as carbon dioxide or bicarbonate. The nitrifiers do not employ the same metabolic mechanisms as those organisms which assimilate organic compounds, and which are used to eliminate BOD* in domestic sewage treatment processes according to the equation:

$$BOD + O_2 \longrightarrow CO_2 + H_2O + \text{new cell material} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

An activated sludge† system can be designed to achieve both BOD removal and nitrification in a single aeration basin. Biological nitrification by the activated sludge process has been applied successfully to ammonia concentrations as high as 500 g/m^3 with greater than 90% removal in a single stage system. Two stage systems have achieved greater than 97% removal at such a high influent level. The optimum conditions for nitrification are 28-32°C (the process ceases below 5°C) and a pH in the range 7.8-8.3. The rate is lowered by the presence of toxic materials such as heavy metals, cyanides, and many organic compounds, and the process is very sensitive to the shock loadings which are likely to occur when it is used to treat industrial waste water.

Air Stripping of Ammonia

The air stripping process for ammonia removal consists of raising the pH of waste water to 10.5-11.5 and providing sufficient air-water contact to strip the

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*Conventional pollution parameters such as BOD and COD are defined in the section on the environmental impact of pollution.

†The activated sludge process consists of aerating the contaminated water in the presence of a flocculated suspension of biological organisms on particulate organic matter.

ammonia gas from solution. The principles used in the design of conventional cooling towers are applicable to the process. There are, however, several disadvantages in the use of cooling towers for stripping ammonia. In situations where low winter temperatures are experienced there may be difficulty in the transfer of ammonia from solution because of its increased solubility. When lime is used to raise the pH of the water, scaling of the tower packing is likely to occur. Finally, if the stripped ammonia is discharged to the atmosphere the overall pollution problem is not really solved.

Biological Denitrification

Under anaerobic conditions nitrate may be reduced or denitrified to gaseous nitrogen. For proper denitrification to occur, an organic source must be present so that the microbes can perform their normal metabolic activities according to the equations:

$$\mathrm{BOD} + H_2O \longrightarrow CO_2 + (H) \quad \ldots\ldots \quad (4)$$

$$(H) + 2NO_3^- \longrightarrow N_2 + 4H_2O + 2OH^- \quad \ldots\ldots \quad (5)$$

If a waste stream containing only inorganic impurities is treated, there will be an optimum amount of organic material which must be added to allow complete denitrification to occur without giving rise to a residual oxygen demand in the effluent. In many industrial processes it is advantageous to treat the waste for nitrate reduction ahead of a BOD removal system. In this way carbonaceous material exerting a BOD in the raw waste is used as the denitrifying carbon source. This reduces the cost of providing an external carbon source (methanol is the most economical source). The aeration volume and power requirement of the subsequent BOD removal system are also reduced because of the BOD reduction in the denitrification system. The denitrification process has been effectively applied to nitrate concentrations as high as 10 000 g/m^3 [93].

Treatment of Nitrogenous Effluents by Ion Exchange

The effluent problems from a nitrogenous fertilizer factory in the USA have been described in some detail[86,94,95] together with a description of some research into possible techniques for reducing nitrogen concentrations in waste waters. The waste stream from the ammonia/nitric acid area of the factory was estimated to contain approximately 100 g/m^3 of ammoniacal nitrogen and 120 g/m^3 of nitrate nitrogen. This stream comprised process condensate, spills and leaks and cooling tower purge water. A significant feature of the waste stream was the high nitrate concentration which must have come from leaks in the nitric acid plant. The ammonium nitrate area waste contained 2 500 and 10 000 g/m^3 of ammoniacal nitrogen and nitrate nitrogen respectively. Again the high concentrations compared with those quoted previously for ammonium nitrate process condensate indicate a significant contribution from process leaks and spills. The solutions are too dilute to return to the processes, and the most obvious method of evaporation to concentrations which could be recycled is ruled out because of the hazards involved in handling contaminated ammonium nitrate. Various methods were therefore investigated to remove or reduce the nitrogenous load into the plant waste stream.

Laboratory studies of ammonia removal on a trickling filter plant indicated that ammonia removal from the waste stream would only approach 20-40%. The maximum efficiency for denitrification was found to be around 80%, and a minimum retention period of 25-30 days would be required.

Experiments on air stripping of ammonia were carried out in a conventional cooling tower, but scaling of the tower packing and the creation of an air pollution problem were regarded as severe disadvantages. Precipitation of ammonia as magnesium ammonium phosphate was investigated, but problems were experienced in removing all the phosphate. Reverse osmosis and selective ion exchange were considered as possible methods for concentration of ammonium nitrate waste streams. The experiments with reverse osmosis were not encouraging, but pilot plant tests on an ion exchange system were very promising. A treatment plant based on ion exchange was therefore installed.

The plant consists of a moving-bed, continuous flow, countercurrent ion exchange system. There are two separate parts to the system; one which is selective for the nitrate ion and the other selective for the ammonium ion. The chemical regenerants are aqueous ammonia and nitric acid. The products from the plant were designed to be 11 tonnes/d of a 20% solution[95] of ammonium nitrate, and demineralized water which could be used as boiler feed or process water.

The unit has not been operating as well as originally hoped. The total nitrogen concentration in the waste water from the plant has been reduced to about 20 g/m^3. This is too high for release to receiving waters, although it can be re-used as cooling water. The concentration of recovered ammonium nitrate has been running at under 15%[96]. This has created some problems in recycling it into liquid fertilizer products where only a limited quantity of additional water can be tolerated. The problems would be even greater in Europe where the market for liquid fertilizers is relatively small. Further concentration of the solution would be required for the production of solid fertilizers. If this were to be done by evaporation, care would have to be taken that the solution did not contain materials which would sensitize the ammonium nitrate and cause an explosion. A particularly dangerous contaminant would be chloride which would create a corrosion problem in addition to the explosion hazard. Ion exchange therefore requires further development as a recovery technique before it can be applied to the abatement of water pollution from a fertilizer factory in the EEC.

Biological Treatment of Effluents in Europe

Major schemes for the biological treatment of effluents, including those from fertilizer processes have been announced by DSM in the Netherlands and BASF in Germany[97]

In both cases nitrogenous wastes from fertilizer processes form an important part of the total aqueous effluent but organic impurities from other chemical processes are also present at high concentrations. DSM have supplied information on the process which they are developing[98,99,100] and this will be described in some detail.

The DSM chemical plants at Geleen consist of four groups of plants producing chemicals. Besides synthetic fertilizers and urea, there is an organic products group (caprolactam, acrylonitrile and melamine), a hydrocarbons group (ethane and propane) and a polymers group (polythenes, synthetic rubbers etc). Waste waters from these plants are discharged into the River Maas (Meuse) along four routes:

Stream 1	ca.2000 m^3/h containing NH_4^+, NO_3^-, PO_4^{3-},COD
Stream 2	ca.800 m^3/h containing COD, NH_4^+, NO_3^-
Stream 3	100-200 m^3/h, mainly household waste and rainwater
Stream 4	ca.200 m^3/h, uncontaminated water from polymer plants.

All these streams are subjected to mechanical clarification. Stream 2, comprising all the waste water from the hydrocarbon and polymer groups and part of the water from the organic products group, is further purified by biological oxidation in a "Pasveer" oxidation ditch.

A Pasveer ditch is an oval channel fitted with aeration rotors which keep the bacterial floc in suspension and supply oxygen for the biochemical reactions which take place. It has a long holding time of 2-3 days and a low sludge loading compared with an activated sludge installation which has a holding time of 3-5 hours and a high sludge loading. The oxidation channel has a large buffering capacity which offers an appreciable advantage for the treatment of industrial effluents. The system can absorb shock loads or surges without serious consequences, while purification in an activated sludge installation would be disturbed[99].

The existing system is only designed for the treatment of bio-degradable organic substances and does not remove nitrogen from the waste water. DSM discharges 10 000 tonne/y of nitrogen into the River Maas, which amounts to 21.5% of the total in the river. The Maas is a rain-fed river with a widely fluctuating flow: in winter, over 1000 m^3/s, and at the end of summer, often as little as 2 m^3/s or less. The total volume of waste water discharge from the DSM plants is nearly 1 m^3/s, so that in the dry season of the year scarcely any dilution of the effluent takes place. With the advent of increasingly severe legislation on the discharge of contaminated waste water, and plans to use the Maas for drinking water supplies, it has become necessary to reduce the discharge of nitrogenous compounds as well as organic substances.

A four-stage process has been designed for the biological purification of the waste water. The first step uses the COD* present in the effluent for reduction of nitrate. The effluent is then subjected to simultaneous nitrification and biological oxidation, leaving a stream polluted only with nitrate ions. This is augmented with a secondary effluent stream, not containing nitrogen, to provide the necessary COD for the third step, which is another denitrification process. The final step subjects a stream containing only COD to biological oxidation to produce an acceptable waste stream for discharge into the Maas. It is intended that steps two and four will be carried out in Pasveer oxidation ditches. Tests have been carried out on a laboratory scale ($1:10^7$), semi-technical scale ($1:10^5$) and, for the last year, in a pilot-scale (1:200). The process is rather more sophisticated than the above description implies but further details are still confidential. It is intended that the full scale plant will be in operation by 1976. The effect of the present and proposed future purification plants on the composition of the overall effluent is summarized in Table 33.

TABLE 33. - Effect of Biological Purification on Composition of Effluent

		flow-rate m^3/h	COD		Ammonia-N		Nitrate-N	
			kg/h	g/m^3	kg/h	g/m^3	kg/h	g/m^3
1972	before purification	3 200	2 200	690	1 000	312	400	125
1972	after BOD reduction in Pasveer ditch	3 200	1 000	312	1 000	312	400	125
1976	before purification	3 200	1 500	470	300	94	200	63
1976	after purification in new plant	3 200	300	94	14	4	10	3

The new installation will have a population equivalent of 2 million. The total investment is at present estimated to be Dfl. 50-60 million (\$18-21 million), with annual costs amounting to Dfl 12-15 million (\$4-5 million). Estimated costs per tonne of nitrogen removed are given in Table 34.

The treatment cost is very dependent upon the cost of the organic material which is necessary for the operation of the process and it is therefore cheaper to remove nitrates than ammonia. If there are no plants on the site of a fertilizer factory producing organic wastes and all the COD has to be purchased as methanol, the cost is approximately twice as high as it would be if all the necessary COD is available in effluents from other (non-fertilizer) plants, essentially free of charge. In practice

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*DSM prefer to discuss the process in terms of the parameter COD, because of its relative ease of measurement. The average COD to BOD ratio on non-sedimented domestic waste water is approximately 2.5.

TABLE 34. - Costs of Nitrogen Removal by Biological Nitrification-Denitrification

Source of COD	Cost per tonne of N removed			
	Ammonia-N		Nitrate-N	
	DFl	$	DFl	$
All COD available in effluent	1 400	500	800	300
COD bought at DFl 60/tonne	2 000	700	1 500	550
COD bought at DFl 150/tonne (methanol)	2 500	900	2,000	700

the situation at most factories will be somewhere in between these two extremes.

Water Pollution Control by Improvement of Existing Plants

The figures in Table 34 show that the cost of biological purification of nitrogenous effluents is high. In situations where legislation is demanding a high standard of purity in the waste water there is therefore a strong economic incentive to reduce the load on a biological purification plant. There are numerous ways in which improvements can be made by means of better plant housekeeping and control. In some instances modifications to processes designed to aid recovery of valuable materials from waste streams will become attractive compared with the cost of biological purification. There will, however, be some highly diluted or contaminated effluents for which biological treatment remains the most efficient process available.

Some examples of the measures which can be taken to minimize the cost of effluent treatment are as follows:

(1) Recirculation of waste water streams.

(2) Installation of monitoring devices which warn operators when water is running to waste e.g. when tanks overflow or test cocks have not been closed.

(3) A general tightening up of discipline among operating personnel.

(4) The size of the purification plant can be minimized by restricting the

volume of water to be treated. This can be done in several ways. The use of indirect condensers will minimize the contamination of cooling water so that it does not require purification. Air cooling can be used whenever possible to reduce cooling water consumption. Finally, the installation of separate drainage systems for waste water which is uncontaminated, water which can be recirculated, and water which must be purified, will greatly reduce the capacity required in the purification plant.

The overall cost of effluent purification can, in some cases, be reduced by employing one of the physical recovery techniques which have been mentioned in the earlier sections of this report. This is illustrated by the data in Table 35, which are calculated assuming biological treatment costs of $700/tonne of ammonia-N and $550/ tonne of nitrate-N. Perhaps the best example is the treatment of the urea plant effluent. Assuming that the high concentration of nitrogen in the raw effluent could be handled in the biological purification plant, the treatment cost would amount to $0.63 per tonne of urea produced. This amounts to twice the cost of discharging the effluent assuming that the penalty is $4.3 (DFl 12) per population equivalent. The hydrolysis/stripping process, on the other hand, can be operated at a cost of $0.21 per tonne of product, and money can therefore be saved by using this process. If biological purification is applied to the residue the overall cost is less than half the cost for biological treatment of the raw effluent, and approximately equal to the penalty for discharge to the river. The final effluent will be of sufficiently high quality to be used as a drinking water supply.

The calculation for the ammonia plant condensate is based upon data in first two lines of Table 1. The lower cost for biological purification would probably apply to European plants. Biological purification is cheaper in this case, particularly so if the steam stripping process uses a reflux column for ammonia recovery.

The cost of purification of ammonium nitrate process condensate is particularly high. Three examples are given in Table 35. The first example is for a plant in which there are two stages of neutralization. The condensate contains up to 0.5% of ammonia and negligible nitrate. It is assumed that the stoichiometric quantity of steam is evolved in the formation of 87% ammonium nitrate solution. Approximately 77% of the condensate could be recycled to the nitric acid plant and this would reduce the cost of purification from $1.12 to $0.25. The cost of recirculation is not available but it is probably quite small. The second example is based upon a contractor's specification for a 500 tonne/day plant in which 0.6 tonnes of condensate contain up to 0.1% free ammonia and up to 0.2% ammonium nitrate. The cost of purification of the raw effluent is lower in this example but the reduction in cost on recycling part of the condensate is not so pronounced because of the larger volume of effluent. The final example is based upon data given for a plant in the USA[95] which uses ion exchange for recovery of ammonium nitrate from the condensate. The only information that is available on the economics of this ion exchange process is that it is possible to recover ammonium

TABLE 35. - Costs for Purification of Aqueous Effluents Containing Nitrogen

Waste Stream	N content, kg/tonne product	Cost of Biological Treatment, $/tonne product	Physical Recovery Treatment	Cost of Physical Recovery, $/tonne product	Cost of Biological Treatment of Residue, $/tonne product
Urea Plant Condensate	0.9(as NH_3)	0.63	hydrolysis/stripping	0.21	0.06
Ammonia Plant Condensate	0.5-1.0(as NH_3)	0.35 - 0.70	steam stripping	0.47 - 0.79	0.02
Ammonium Nitrate Condensate					
1. Two-stage neutralizer[81]	1.6 (as NH_3) no NO_3	1.12	recycle to HNO_3 plant	not known probably small	0.25
2. Contractors data for 500 tonne/d plant	0.7 (as NH_3) 0.2 (as NO_3)	0.60	"	"	0.30
3. Plant in USA[95]	1.0 (as NH_3) 1.0 (as NO_3)	1.25	ion exchange	0.8 recovered as product, total cost not known	0.18

nitrate to the value of $0.8 per tonne of product. It must be remembered, however, that the ammonium nitrate solution produced in the ion exchange process would need to be concentrated further before it could be processed into a solid product. It is doubtful whether ion exchange could reduce the high cost of biological purification in this case. Information from another source (see Table 52) indicates that the cost of ion exchange is very high.

There is considerable variation in the cost of purification of the ammonium nitrate process condensate depending upon the concentrations of the impurities. Relative to the other nitrogenous effluents the cost of biological purification is high. It can be reduced by recycling part of the condensate to the nitric acid plant, provided suitable precautions are used to ensure safety.

GRANULAR COMPOUND AND COMPLEX FERTILIZERS

Process Descriptions

Compound and complex fertilizers are homogeneous mixed fertilizers containing two or all of the primary components. The term complex fertilizers is normally used to describe nitrophosphates, produced by the attack of nitric acid on phosphate rock. Manufacture of nitrophosphates is chiefly carried out in Germany, the Netherlands and Scandinavia, and was popular until a short time ago in France. It is estimated that 20-25% of the total NPK production in the EEC is made by this route[36]. The other basic route to compound fertilizers is the granulation of a slurry of ammonium nitrate, ammonium phosphate and potassium chloride. Most compound and complex fertilizers are produced in granular form because the process is more flexible than prilling for the production of a range of different formulations, There is, however, some production of prilled NPK fertilizers.

The production of nitrophosphate fertilizers is based upon the reaction:

$$Ca_{10}F_2(PO_4)_6 + 20\ HNO_3 \rightarrow 6\ H_3PO_4 + 10\ Ca(NO_3)_2 + 2HF$$

If the resulting solution is simply ammoniated, dried and granulated, essentially all the phosphate would be present as water-insoluble dicalcium phosphate and the product would contain enough hygroscopic calcium nitrate to seriously impair its handling characteristics. Technological developments have therefore focussed on the removal of calcium nitrate.

Several processes are in use which are based upon the original Odda process, in which calcium nitrate is removed by cooling and crystallization. The calcium nitrate is prilled and sold as a by-product (15% N) or treated with ammonia and carbon dioxide to form ammonium nitrate and calcium carbonate. These latter two products can either be sold separately, or together as calcium ammonium nitrate. The remaining solution is ammoniated, and granulated or prilled to produce fertilizers containing ammonium nitrate, dicalcium phosphate and ammonium phosphate. The ratio of ammonium to dicalcium phosphate depends upon the degree of calcium removal and determines the water-solubility of the product. Most commercial processes have been aimed at a product containing 30-40% water soluble phosphate. A flow diagram of an Odda-type process is shown in Fig.11.

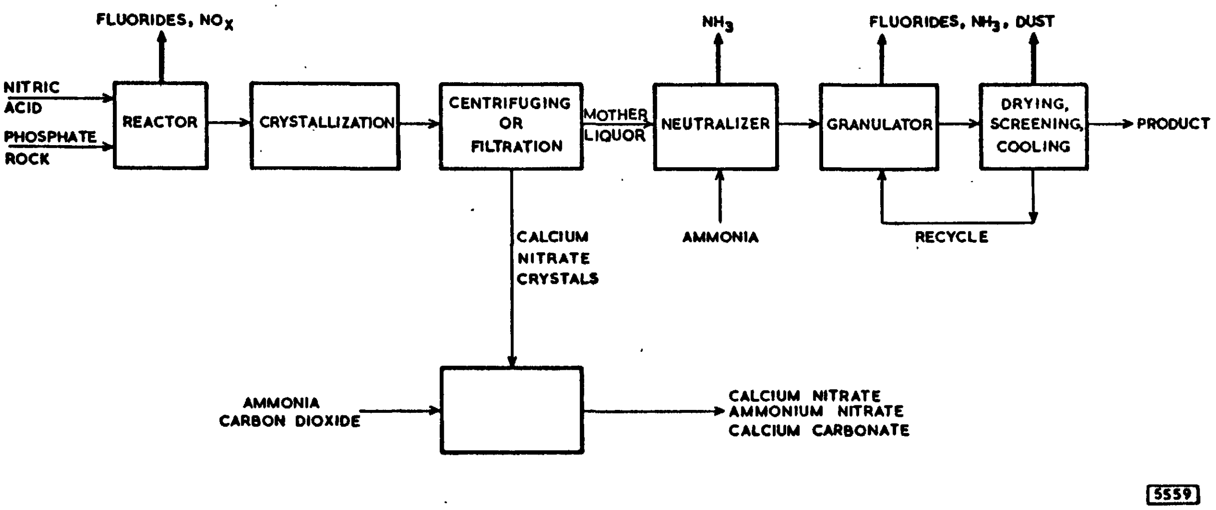

FIG. 11 FLOW SHEET FOR AN ODDA - TYPE PROCESS

An alternative approach has been the use of additives to convert the calcium nitrate into a product which is easier to remove, or which need not be removed at all. One method is to add a soluble sulphate to precipitate calcium sulphate, but this introduces a disposal problem unless the calcium sulphate is left in the product. Alternatively, the calcium sulphate may be reacted with ammonia and carbon dioxide to regenerate ammonium sulphate and precipitate calcium carbonate, which may be a less undesirable by-product. Another possibility is the addition of phosphoric acid so that ammonium phosphate is formed in the ammoniation. The usual practice is to formulate for 40-50% water-solubility. These processes are known as sulphonitric, carbonitric and phosphonitric processes respectively.

A large part of compound fertilizer production is made by a process which was developed by the Tennessee Valley Authority (TVA). The basic process produces di-ammonium phosphate. Phosphoric acid is neutralized in a pre-neutralizer with anhydrous ammonia to a $NH_3:H_3PO_4$ molar ratio of about 1.3, a point near the maximum solubility of the system. The slurry produced is fed to a rotary drum 'ammoniator-granulator' together with recycled fines. Additional ammonia is added to give a molar ratio of 2.0, a point of minimum solubility. Excess ammonia is recovered by scrubbing the exhaust gases with the phosphoric acid feed to the pre-neutralizer. A large variety of grades of fertilizer, rich in di-ammonium phosphate, can be produced by neutralizing with ammonium nitrate solutions rather than anhydrous ammonia, substituting sulphuric acid for part of the phosphoric acid, or adding solid ingredients, such as potassium chloride to the granulator. The process is illustrated in Fig. 12.

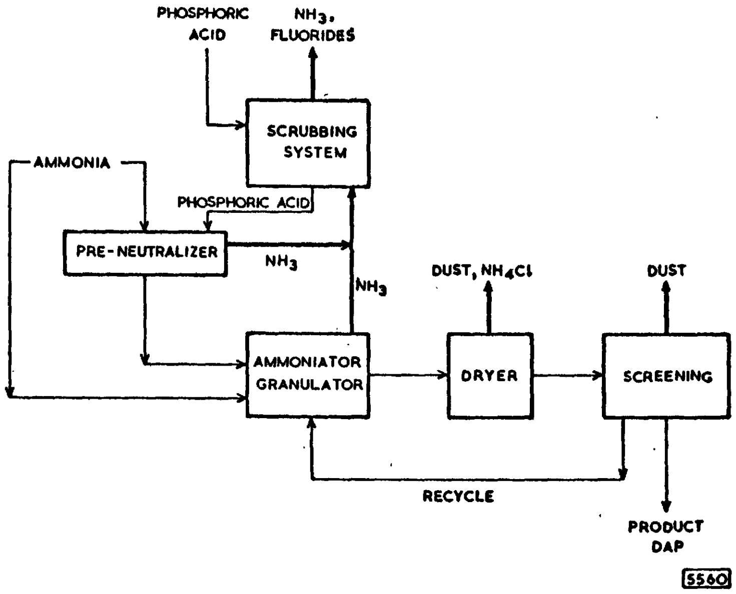

FIG.12 FLOW SHEET FOR DAP PRODUCTION BY THE TVA PROCESS

In the UK the bulk of high-analysis compound fertilizers is made from ammonium nitrate, ammonium phosphate and potassium chloride by a slightly different process. Ammonium phosphate is produced in one or two stages of neutralization, depending upon the grade required. This is fed, together with concentrated ammonium nitrate and solid potassium chloride into a granulator, which is usually a twin-shafted paddle mixer (a pugmill or blunger) or a rotating drum.

There are various designs of granulator in use[101]. On a world-wide basis the most frequently used is the TVA ammoniator-granulator. It has a reputation for flexibility, having been used for the production of superphosphates, ammoniated superphosphates, and nitrophosphates in addition to NPK compounds based on ammonium phosphate. The granulator, drier, screens and crusher, together with the associated conveying equipment constitute the 'granulation loop'. By its very nature the granulation process involves recycle of material. To maximize plant output it is mostly desirable to have a low recycle ratio.

Many companies operate granulation plants which produce compound fertilizers from primary fertilizer products such as superphosphate, ammonium phosphate, ammonium nitrate and potassium chloride. The component materials are simply weighed, mixed and granulated in a conventional granulation loop.

Sources of Pollution

It is difficult to generalize about the effluents from a compound fertilizer plant because of the large number of variations in the processes operated and the different formulations that are produced. The different processes do have certain features in common, however, in that the nature of the solid, liquid or gaseous effluents is similar, although the quantities might vary considerably. The solid effluents are fertilizer dusts, which can be recovered by dry or wet cleaning. The gaseous effluents are ammonia, nitrogen oxides, and fluorine in the form of HF or SiF_4. The liquid effluents contain dissolved fertilizers and fluorine from the process itself, or from the scrubbers used to control the gaseous effluents. Control of the loss of ammonia and fertilizer dust reduces the loss of raw materials and improves the yield of the plant, while control of fluoride emissions is purely for the protection of the environment.

Air Pollution

Most of the available information refers to granular fertilizers based upon ammonium phosphate. It has already been pointed out that ammonia losses in the neutralization of phosphoric acid can be high when the molar ratio $NH_3:H_3PO_4$ is greater than 1.0. In a TVA-type plant making a 17-17-17 NPK fertilizer the preneutralizer is operated at 140-150°C[39]. At these temperatures and at a molar ratio not exceeding 1.45, between 8 and 12% of the total ammonia introduced can escape. Only small quantities of fluorine are released, but the gases must be scrubbed to recover the ammonia. The phosphoric acid feed is often used as the scrubbing liquid. If the pH is less than 4.5-5.0 and the temperature higher than 70°C fluorine-containing gases can be stripped from the phosphoric acid. The best ammonia recovery is obtained under these conditions so that fluorine stripping often occurs. The quantity of fluorine stripped has been quoted as being in the range 0.4-4 kg/tonne of P_2O_5[39,102]. For a production of 1000 tonnes/d of 17-17-17, 4 kg/tonne of P_2O_5 corresponds to 680 kg/d of fluorine waste.

In the process much used in the UK the first stage of neutralization is carried out at a molar ratio of less than 1.0 and ammonia losses are negligible. The second stage is carried out at a molar ratio of 1.4-1.6. Here ammonia losses are considerable and the ammonia must be recovered and returned to the process.

Air is circulated through the slurry in the granulator. At the outlet this air will contain moisture, fertilizer dust and ammonia. Again ammonia losses increase with the molar ratio $NH_3:H_3PO_4$ in the product. If the molar ratio is very high (>1.85) they may reach up to 15% of the ammonia introduced into the granulator. The quantities of fluorine released are very small.

The main effluent from the other parts of the granulation loop is fertilizer dust, in amounts varying with the humidity, granulometry and formula of the fertilizer. Most dust particles are between 0.05 and 0.5 mm in diameter. There is also a tendency, particularly in the drier, for the formation of ammonium chloride. This may be due to reactions between sulphuric acid and potassium chloride to form hydrogen chloride, which reacts with ammonia, or between ammonium salts and potassium chloride. Ammonium chloride sublimes at 150°C so that if the drier is operated at a higher temperature than this the formation of a dense white plume is likely. The size of the ammonium chloride particles is of the order of 10^{-3} mm and they are very difficult to remove by scrubbing. For example, tests on a plant in the USA showed losses of ammonium chloride of 0.1 kg/tonne of product from the ammoniator exhaust and 0.2 kg/tonne from the drier and cooler exhaust[103]. The scrubber on the drier and cooler exhaust only removed 50% of the ammonium chloride. Studies on another plant in the USA showed that the use of superphosphoric acid (76% P_2O_5) in fertilizer formulation reduced the amount of chlorides in the exit gases from an ammoniator-granulator from 1.8 kg/tonne of product when sulphuric acid was in the formulation to only 0.002 kg/tonne when superphosphoric acid was used[104].

In nitrophosphate processes fluorine will be released in the attack of nitric acid on phosphate rock. Attack is very rapid and only a small amount of fluorine is evolved, i.e. about 5% of the total fluorine in the rock. This fluorine is easily removed by wet scrubbing and the concentration of fluorine emitted to the atmosphere can be as low as 10 mg/m^3, corresponding to a loss of a few grams of fluorine per tonne of product. Most of the remaining fluorine will be carried through into the fertilizer product, but if calcium is precipitated as calcium sulphate or calcium carbonate some calcium fluoride will also be removed in the filtration.

There will also be some evolution of nitrogen oxides in the reactor if the phosphate rock has a high organic content. Nitrogen oxide emissions can be expected, for example, to be lower from Kola rock than from Florida or Morocco rocks. Ammonia will be released in the neutralizer. If the gases from the neutralizer go to a direct contact barometric condenser ammonia will dissolve in the condenser water. In a recirculating cooling water system the purge can be used to wash the gases from the reactor.

The remainder of a nitrophosphate process will consist of a granulation loop and the problems will be similar to those encountered in an ammonium phosphate process. The quantities of dust and gas emitted will depend upon the process conditions.

Some data on emissions to the atmosphere after scrubbing from NP and NPK fertilizer plants are given in Table 36. Not all of these plants are in the EEC, but the quantities in the Table serve to illustrate the points discussed above. Fluoride losses (in kg/tonne product) from nitrophosphate processes tend to be considerably smaller than from ammonium phosphate-based processes. Losses of ammonia and dust can be quite high and this probably reflects the relative inefficiency of the scrubbing systems used. The Norwegian figures are maximum emissions which have been set by the authorities for two plants. The other data are results of actual measurements of emissions. The overall conclusion from Table 36 is that there can be wide variations in the emissions from different plants depending upon the process and the efficiency of the scrubbing system. The formula of the fertilizer product may also be important. The concentrations of pollutants emitted to the atmosphere can vary widely depending upon the extent of dilution with air.

TABLE 36. - Emissions to the Atmosphere from NP and NPK Fertilizer Plants

Process and Location	Total Emission to Atmosphere in kg/tonne of product (A) and mg/m^3 (B)														Reference
	Ammonia		Ammonium Nitrate		Nitrogen Oxides as N		Fluorides as F		Chlorides as Cl		Sulphur Dioxide		Dust		
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	
Nitrophosphate Process in Germany	0.03-0.12	50-200	-	-	0.14-0.21	500-700	0.015-0.03	50-100	-	-	-	-	0.16	40	-
Carbonitric Process in Sweden	1.05	10	-	-	0.48	55	0.005	0.5	-	-	0.03†	2.5	1.19	135	92
Odda Process in Sweden	0.02	3	-	-	0.03	5	0.004	1	-	-	-	-	0.20	30	92
Odda Process in Norway, Plant 1	0.60	-	-	-	0.45	-	0.015	-	-	-	0.09	-	0.47	-	105
Odda Process in Norway, Plant 2	0.70	-	2.57	-	-	-	0.005	-	-	-	0.27	-	3.0	-	105
NPK via Ammonium Phosphate:															
in Ireland Plant 1	2.8	-	-	-	-	-	0.02-0.5	5-150	-	-	-	-	-	-	-
in Ireland Plant 2	-	280-560	-	-	-	-	-	-	-	-	-	-	-	400-1000	-
in Sweden	1.10	180	-	-	0.33	56	0.12	20	0.26	44	1.17ϕ	197	0.43	72	92
DAP Plant in France	3.3*	50-2000	-	-	-	-	0.15	2-50	-	-	-	-	-	-	61
DAP Plant in USA 1	7.5	-	-	-	-	-	0.06	-	-	-	-	-	-	-	59
2	1.2	-	-	-	-	-	0.05	-	-	-	-	-	-	-	
3	-	-	-	-	-	-	0.03	-	-	-	-	-	-	-	
4	0.05	-	-	-	-	-	0.20	-	-	-	-	-	-	-	
5	0.14	-	-	-	-	-	0.15	-	-	-	-	-	-	-	
Granulation Plants in Ireland 1	-	-	-	-	-	-	0.04	20	0.67	300	-	-	-	-	-
2	-	-	-	-	-	-	-	<325	-	-	-	-	-	800-1600	-

*NH_3 gas 85%, ammonium salts dissolved in droplets of water 15%

ϕ25% of SO_2 from boiler, remainder from drier, presumably from coating agent.

†SO_2 from oil used as coating agent

Water Pollution

Water pollution from a compound fertilizer plant usually arises from the discharge of liquor from scrubbers used to control air pollution. The economics of the process demand that ammonia losses should be kept to a minimum, so that there is a strong incentive to recycle the scrubber solution to the process. This is not so with fluoride emissions. Again it is difficult to generalize because the scrubbing procedure and the amount of recycling will vary from plant to plant. In some cases, when the scrubbing system has been primarily designed to remove fluorine, a common scrubber may be used to control dust and other gases as well as fluorides. In this way the equipment is simplified and investment costs are lowered, but water pollution will necessarily be increased. The gases from a granulator may be diluted with a large amount of air, making recovery less efficient. It is therefore desirable that a separate scrubber should be used so that a high degree of recovery can still be achieved in other parts of the process.

Fluorine scrubbing in phosphate production has been quoted as requiring 2.1-12.6 m^3 of water per tonne of product[4]. The fluoride concentration varied between 25 and 250 g/m^3 and the ammonia concentration varied between 5 and 50 g/m^3. These figures correspond to fluoride losses of up to 3.75 kg/tonne of product and ammonia losses of up to 0.75 kg/tonne of product. The scrubber solution from the neutralizer on a phosphonitric process in Belgium contains 50-100 g/m^3 of ammonia, a few g/m^3 of nitrate and practically no phosphate. Table 37 summarizes data on the composition of the aqueous effluent from a number of NPK fertilizer plants. The main point of interest is the much smaller quantity of fluorides discharged to waste in the nitrophosphate processes compared with di-ammonium phosphate processes.

Control Techniques

Granulation plants are notoriously dusty, and precautions must be taken to recover the fertilizer dust and return it to the process. The main burden of dust recovery is taken by batteries of high efficiency cyclones. The efficiency of cyclones depends upon the size of the particles of dust:

Particle size	Efficiency
<2.5 µm	68%
<5 µm	85%
<10 µm	95%
<25 µm	99%

Yields are usually between 94% and 98.5% but they vary according to the granulometry of the dust. This may vary enormously for different grades of fertilizer. Dust losses may be very high for some grades due to the fineness of the dust. For example, some typical cooler gas dust burdens can be quoted[106].

TABLE 37. - Aqueous Effluents from NPK Fertilizer Plants

Process and Location	Quantity of water in m^3/tonne of product	Total Aqueous Effluent in kg/tonne of Product (A) and g/m^3 (B)								Reference
		Ammoniacal Nitrogen as N		Nitrate Nitrogen as N		Phosphates as P		Fluorides as F		
		A	B	A	B	A	B	A	B	
Nitrophosphate Process in Germany:										
Acid Attack	2.5	-	-	5.0	2000	2.5	1000	0.05	20	-
Granulation Loop	3.0	1.0	330	0.01	3.3	1.2(as NPK)	400	-	-	-
Carbonitric Process in Sweden	11.9	0.68	55	0.34	28	0.05	4	0.05	5	92
Odda Process in Sweden	20.0	0.67	33	0.75	38	0.09	5	0.42	21	92
Odda Process in Norway,										
Plant 1	-	2.16	-	1.27	-	0.23	-	0.33	-	105
Plant 2	-	1.60	-	3.00	-	1.03	-	0.13	-	
NPK via Ammonium Phosphate in Ireland	-	-	1000 (total N)	-	-	-	1700	-	180	-
Granulation Plant in Ireland	-	-	180 (total N)	-	-	-	380	-	110	-

TABLE 38. - Dust Content of Gases from a Granulation Plant

Product	Dust Burden, g/m^3	
	into cyclone	out of cyclone
ammonium sulphate nitrate	44.1	0.48
	24.4	0.64
single superphosphate	99.4	1.33

Recycling of fertilizer to the process is very much simpler from a dry cyclone than from a wet scrubber. It is therefore important that the cyclone is operated at the pressure drop which gives the optimum efficiency. This is particularly important when there is a dry discharge to the stack, which is preferred by some operators because of the absence of a steam plume. In the UK an efficiently run cyclone can meet the Alkali Inspectorate's provisional requirement of a dust burden less than 0.46 g/m^3. In practice wet scrubbing is required in addition to meet the requirements for acidity of the stack gases and this reduces the dust burden to less than 0.1 g/m^3. Frequently two scrubbers are used. The liquor from the first scrubber, or recovery scrubber, may be recycled to the process or discharged to drain. The second, or abatement scrubber uses a large quantity of water (e.g. 1200 m^3/h) to reduce the exit gas temperature and avoid a steam plume.

In order to remove particles smaller than 5 μm at efficiencies greater than 90% it is necessary to use a wet scrubber after the cyclones. A popular choice of scrubber for this duty is the irrigated target or impingement plate scrubber. The dirty gases pass through perforated trays with an irrigated target set above each perforation. The gas stream is divided into many tiny jets which impinge on the target at high velocity. Dust removal efficiencies higher than 95% for 2 μm particles are obtained at a pressure drop of around 10-15 mm WG. The cyclonic spray tower has a rather lower efficiency, but it can be operated at a very low pressure drop. Efficiencies of over 99% can be obtained for particles in the 1-5 μm size range by using Venturi scrubbers, which are also effective for removing sub-micron fume such as ammonium chloride. Running costs are high, however, because of the high pressure drop (40-50 mm WG).

Impingement plate scrubbers, or the simpler jet impingement scrubber where a small number of jets of gas play upon the surface of the liquid, are commonly used for recovery of ammonia from the preneutralizer. Recirculated phosphoric acid is often used as the scrubbing medium in both the ammonia recovery and the dust recovery scrubbers, Fluorides must be treated in a separate circuit, using water as the scrubbing medium. Suitable scrubbers for fluoride removal have already been discussed.

It is possible in a modern fertilizer plant to reduce emissions to the atmosphere to a very low level, and to eliminate discharge of aqueous effluents by recirculation of scrubber liquors, with the exception of the effluent from the fluorine washer. A system designed for this purpose has been described by Barut and Schwob[39]. It is illustrated in Fig. 13. Phosphoric acid is recirculated via the preneutralizer scrubber, recovering 99% of the ammonia in the gases from the preneutralizer. These gases proceed to a scrubber where fluorides are removed by solution in water. Efficiency is greater than 95% with a large flow of once-through water. The flow can be reduced by recycling but the efficiency is reduced slightly. Fresh water and phosphoric acid are used to scrub the gases from the granulator. This scrubber solution then washes the dust from the air from the drier. The solution is then recirculated to the granulator and pre-neutralizer. Dust-laden air from the screens and associated equipment is scrubbed with water in a separate scrubber. Only the water from the fluoride scrubber is discharged to drain. The dust-laden gases, with the exception of those from the granulator, which have a high steam content, pass into high efficiency cyclones before scrubbing. The dust is recovered and returned to the granulator.

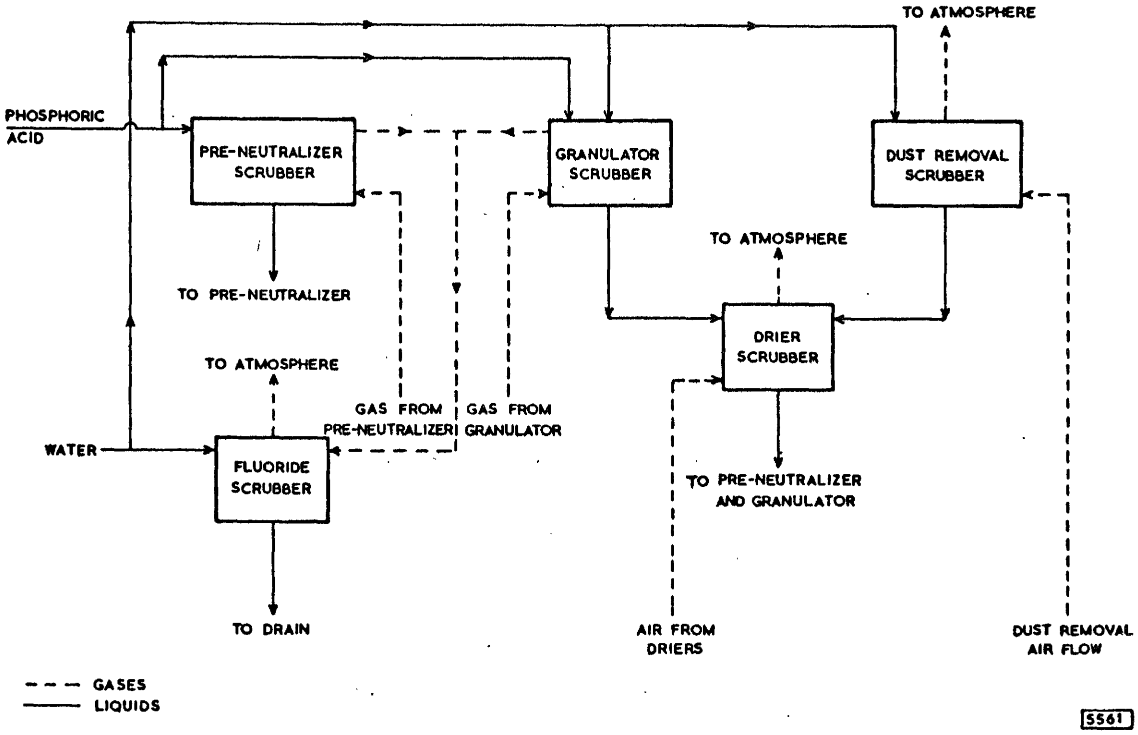

FIG.13 SCRUBBER SYSTEM FOR POLLUTION CONTROL IN A COMPOUND FERTILIZER PLANT

With a system of this type it is possible to achieve very low levels of emission from a compound fertilizer plant. The system would require careful control to ensure that the operation of the scrubbers does not upset the water balance in the process, and operation of the plant would probably be much more difficult. Table 39 shows the emission levels calculated for a 1000 tonne/d output of 17-17-17 fertilizer.

These emission levels are achieved without causing water pollution, with the exception of the water from the fluorine scrubber. It should be pointed out, however,

TABLE 39. - Emissions to the Atmosphere from a Compound Fertilizer Plant with Modern Control Equipment

	Scrubber Efficiency %	Emission to Atmosphere, kg/tonne product		
		ammonia	fluoride	dust
preneutralizer	99	0.06	-	-
ammonia recovery	95	-	0.004-0.04	-
granulator	95	0.08	-	-
dust recovery:				
cyclones	95	-	-	2.4
dust scrubber	99	-	-	0.02

that the fertilizer industry considers the ammonia and dust emissions in Table 39 to be low by a factor of at least ten, and not achievable in practice.

Only a limited amount of economic information is available about this system. It was estimated that the cost would amount to 11% of the capital cost of a 1000 tonne/d plant. Apart from the fluorine scrubber it is claimed that the units are quickly written off but it has been suggested to the author that the heat requirement to recover all the effluents free of water would be prohibitive in terms of cost. The value of the recovered materials is summarized in Table 40, assuming an output of 1000 tonne/d of 17-17-17 fertilizer.

TABLE 40. - Estimated Value of Materials Recovered in Scrubbing Compound Fertilizer Plant Off-gases

Material Recovered	Rate of Loss, kg/tonne of product	Value of Material, francs/tonne	Recovery Efficiency, %	Amount Saved, francs/year
Ammonia from Preneutralizer	6.0	220	99	431 000
Ammonia from Granulator	1.7	220	94	116 000
Fertilizer Dust	48	240	95 (cyclones)	3 612 000
			99 (scrubbers)	188 000

The value of ammonia has been adjusted to be consistent with the value assumed elsewhere in this report. The value of the recovered materials amounts to 13.2 francs ($3.00) per tonne of product. It is noteworthy that 83% of the recovered value is attributable to the dry cyclones. This part of the system can probably be regarded as an essential feature for economic operation of the plant, rather than as a pollution control measure. Unfortunately information is not available on the extent to which the value of the recovered material in the wet scrubbers, $0.50/tonne of product, offsets the running costs of the equipment.

Some relevant information, is, however, available from other sources. In the USA the EPA has included di-ammonium phosphate plants in its study of the economic impact of air pollution standards on the phosphate fertilizer industry[66]. As in the case of granulated triple superphosphate plants, a combination of scrubbers was considered, which are designed to remove ammonia and particulates on the one hand, and fluorides on the other. Engineering specifications for a plant designed to achieve fluoride emissions of less than 0.03 kg/tonne of P_2O_5 are given in Table 41, and the estimated capital and annual costs which were calculated for two plant capacities are shown in Table 42. These cost estimates do not include a contribution from the provision of cyclones. They do include the costs of the fan, pipework and the stack as well as the basic scrubber costs.

These plants and the compound fertilizer plant previously discussed are not strictly comparable but the processes are similar and control costs should be of the same order of magnitude. In spite of the different methods of estimation the value of the recovered materials in both cases comes to about $0.50/tonne of product. This offsets a considerable part of the total cost of pollution control in large plants in the 1000-1600 tonne/d range. No information is available for smaller plants, but pollution control can be expected to be more expensive as the capacity of the plant decreases. The use of three separate scrubbers for fluoride removal in the DAP plant is not essential, but if suitable interconnecting ducts are provided it is possible to re-route the off-gases in the event of equipment failures. The recirculation of scrubbing liquors to recover raw materials means that the disposal of the liquor from the fluoride scrubbers is the only water pollution problem. The comments made previously about the operation of complex scrubbing systems also apply here.

Many plants have considerably less sophisticated scrubbing systems. As an example, one 600 tonne/d granulated NPK fertilizer plant uses two impingement plate scrubbers, one of which scrubs the gases from the pre-neutralizer and ammoniator-granulator while the other scrubs the drier and cooler exhaust gases after they have passed through cyclones. Recycled 50% P_2O_5 phosphoric acid is used as the scrubbing agent in both scrubbers. The replacement value of the pollution control equipment on this plant is about £60 000, and for a gas flow of 77 000 m^3/h the power requirement is estimated to be about 44 kW. The estimated cost of control, without credit for recovered material, comes to £0.1 or $0.25/tonne of product. The net cost of control must therefore be very low in this plant. There is no separate fluoride scrubber, however, and fluoride losses can be as high as 0.5 kg/tonne of product. Most of the fluoride is in the particulate form and 60% of the particles are smaller than 0.5 µm.

TABLE 41. - Engineering Specifications for Estimating Air Pollution Control Costs for DAP Plants

Plant Capacity	1000 tonne DAP/d		1600 tonne DAP/d	
	Ammonia and Particulate Scrubber*	Fluoride Scrubber†	Ammonia and Particulate Scrubber*	Fluoride Scrubber†
A. Reactor-Granulator				
Gas to Scrubber, m^3/h at 77°C	68 600	65 000	109 700	104 600
Moisture Content %	40	41	40	41
B. Drier				
Gas to Scrubber, m^3/h at 82°C	95 500	91 700	152 600	146 600
Moisture Content %	35	36	35	36
C. Cooler and Transfer Points				
Gas to Scrubber, m^3/h at 60°C	60 000	58 600	96 000	93 800
Moisture Content %	3	4	3	4

*Scrubbing medium 30% H_3PO_4

†Scrubbing medium gypsum pond water

TABLE 42. - Capital and Annual Control Costs for Di-ammonium Phosphate Plants

Plant Capacity	1000 tonne DAP/d		1600 tonne DAP/d	
Costs in $	Ammonia and Particulate Scrubber	Fluoride Scrubber	Ammonia and Particulate Scrubber	Fluoride Scrubber
A. Reactor Granulator				
Capital	155 000*	60 000	210 000*	83 400
Total Annual Cost	62 500	23 000	87 400	32 100
B. Drier				
Capital	162 000†	80 000	225 000†	111 000
Total annual Cost	82 000	30 800	120 000	43 000
C. Cooler and Transfer Points				
Capital	118 000†	57 000	164 000†	79 200
Total Annual Cost	57 000	22 100	83 000	30 800
Summary				
Total Capital, $	632 000		873 000	
Total Annual Cost, $/y	277 400		396 300	
Control Cost, $/tonne DAP	0.84		0.75	
Control Cost with NH_3 credit $/tonne DAP	0.38 Ø		0.29 Ø	

*Two-stage cyclonic scrubber

†Venturi-cyclonic scrubber

ØValue of ammonia taken as $50/tonne. Recovered ammonia is estimated as 40 kg/tonne of ammonia feed, which is equivalent to 9.1 kg/tonne DAP (18-46-0), for all sources combined. The value of recovered ammonia is therefore $0.46/tonne of product.

Another 600 tonne/d plant uses two abatement scrubbers (one of which is fitted to the condenser on the neutralizer of an ammonium nitrate unit which is integral with the plant) to avoid the formation of steam plumes. The running cost of these two units amounts to £43 000 per annum, so that the cost of control is £0.36 or $0.90/tonne of product.

It is preferable to so design the dryer that ammonium chloride fume formation is avoided. Once formed, ammonium chloride fume is not easily controlled. Impingement scrubbers are not very effective, and Venturi scrubbers are expensive to run. A plant in the USA obtained 95% removal of ammonium chloride in a Venturi scrubber on the ammoniator exhaust[103]. The cost of operating this unit, designed for an air flow of 12 000 m^3/h amounted to $0.10 per tonne of product. The air flow from the dryer exhaust was much higher and ammonium chloride fume was not controlled.

Summary

The two basic routes for the manufacture of compound fertilizers are the nitrophosphate processes and the ammonium phosphate-based processes. Losses of nitrogen, mainly as ammonia, and fertilizer dust from the granulation loop are common to both processes. Fluoride emissions also occur, but these are less serious in the nitrophosphate processes. On the other hand, nitrogen oxides may be released in the attack of nitric acid on phosphate rock, a problem which does not arise in the ammonium phosphate processes.

Because of the wide variation in processes and the formulations produced it is difficult to define a typical effluent. There is a strong economic incentive to reduce losses of ammonia and fertilizer dust to a minimum. It is possible to design a suitable system of cyclones and scrubbers which will control the losses to the atmosphere from both types of process, and recycle the recovered material. Emissions of ammonia and dust from a TVA-type plant producing 1000 tonne/d of 17-17-17 fertilizer, fitted with this washing system would be expected to amount to 0.14 kg and 0.02 kg respectively/tonne of product, although the fertilizer industry considers that 1.4 kg and 0.2-0.4 kg would be more realistic figures. Fluoride emissions can be controlled by a simple scrubber but this gives rise to an aqueous effluent. The cost of this system is 11% of the capital cost of the plant.

The net cost of pollution control in a similar scrubber system designed for use in a DAP plant has been estimated to vary between $0.38/tonne of DAP in a 1000 tonne/d plant and $0.29 in a 1600 tonne/d plant. The cost of operating the less sophisticated systems which are commonly used is probably very low, but it is increased considerably if abatement scrubbers are incorporated to avoid the formation of a steam plume.

MISCELLANEOUS POLLUTION PROBLEMS

This section gathers together a number of topics which are considered to be worthy of brief consideration. The selection of topics has been somewhat arbitrary. For example, atmospheric pollution from the combustion of fuel in furnaces and boilers has not been included because it has been extensively discussed elsewhere. Occasional accidents which may occur in the fertilizer industry, such as leakages from storage tanks, are also not discussed because it is not possible to make useful generalizations about such accidents. One type of accident which is peculiar to the fertilizer industry has been included, however, and this is the possible occurrence of self-sustaining decomposition of compound fertilizers.

Contamination of Cooling Water and Boiler Water

Cooling Water

There are basically three types of cooling system used in the chemical industry. In a once-through system large volumes of water are used and the water is returned to its source without any appreciable contamination. The only pollution problem is the temperature increase of the water. Totally enclosed cooling systems are sometimes used. Once filled, the system requires very little make-up water, and very high quality water can be used to prevent scaling. There is no purge from the system and toxic corrosion inhibitors can be used at high concentrations. The most common form of cooling system used in industry, however, is the open evaporative recirculation system employing cooling towers. Under average conditions, a rough rule is that a fall in temperature of 7°C in the cooling tower corresponds to a loss by evaporation of 1% of the water circulated. There will be a corresponding increase in concentration of all substances in solution, and it is therefore necessary to remove a proportion of the circulating water and add a make-up of fresh water in order to maintain the total dissolved substances in the water at an acceptable level. This "purge" or "blowdown" stream forms a waste stream which may be contaminated with a variety of chemicals.

The composition of the purge water will depend upon the feed water composition, cycles of concentration, process leaks, soluble materials in the atmosphere around the cooling tower, and materials added to the cooling water for corrosion, scaling and biological growth control.

Suspended solids may be inherent in the raw water or arise from atmospheric pick-up in the tower and corrosion within the system. They tend to deposit and impair heat transfer processes, and they may encourage corrosion and add to pumping costs. They may be removed by filtration or chemical dispersants may be added to keep insoluble materials in suspension and allow their removal in the purge. Materials used as dispersants include lignosulphonate, polyacrylates, polyacrylamides, phosphonates and

—phosphoric acid esters[107].

Deposits can also occur in cooling systems as a result of bacterial action and the growth of algae and fungi. This problem may be particularly troublesome in the fertilizer industry where the water is likely to contain nutrients such as ammonia and phosphates. The most widely used method of control is chlorination, which is effective and cheap. Chlorine is an oxidizing agent and will react with other impurities in the water. Of particular concern is the reaction with ammonia to form chloramines, which are highly toxic to fish. Alternatively a non-oxidizing biocide can be used. A number of organic materials are available, including acrolein, tertiary butyl hydrogen peroxide and bromo-nitro-styrene[107]. These materials are all toxic and should be neutralized with sulphite before discharge.

Deposits can arise from the crystallization of inorganic salts such as calcium carbonate, calcium sulphate and magnesium hydroxide. The presence of these salts determines the number of concentration cycles that are acceptable. With soft water a concentration of 6-8 times is possible, but with many bore-hole and mine waters, which have a high degree of bicarbonate hardness, even a two-fold concentration gives rise to problems. Sulphuric acid is often added to lower the pH and destroy the bicarbonates. This will reduce the volume of the purge, but will give rise to a significant concentration of sulphate in the waste stream. Too low a pH gives rise to serious corrosion problems, but where a corrosion inhibitor is also present it is possible to virtually eliminate scaling by reducing the pH to about 6.5.

The atmosphere around a cooling tower in a fertilizer factory is likely to contain a number of soluble species which can be absorbed by the water passing through the tower. Sulphur dioxide, sulphur trioxide, ammonia, nitrous gases and fertilizer dusts can all contribute to the impurities in the waste stream from the cooling system.

The presence of all these contaminants, as well as dissolved oxygen, in the cooling water, contributes to the problem of corrosion in the cooling system. It is therefore standard practice to use corrosion inhibitors to protect metal surfaces in the system. Chromate salts have been used for many years and are still the basis of many of the formulations currently used. Older systems used chromate alone for anodic protection. A high concentration (200-500 g/m^3 as CrO_4) was necessary, and very few systems of this type are still in use except for totally enclosed systems. Modern practice is to use a combination of anodic and cathodic inhibitors. A combination of zinc and chromate, for example, enables a much lower concentration of the highly toxic chromate to be used. A typical system would contain 20-25 g/m^3 chromate and 1-5 g/m^3 zinc. Removal of chromate from the waste steam is expensive and there has been some decline in the use of zinc/chromate inhibitors. Their use is still favoured, however, where untreated effluent can be discharged to an estuary or the sea.

The most successful alternative to chromate is a zinc/phosphonate inhibitor containing 4-6 g/m^3 zinc and 10-30 g/m^3 phosphonate, depending on the hardness of the water. The use of zinc/polyphosphate is declining because of the possibility of reversion to orthophosphate and the subsequent precipitation of calcium phosphate. Although regulations covering the discharge of zinc are usually less restrictive than for chromium, zinc is still a very toxic metal. There has been a great deal of research into the use of less toxic corrosion inhibitors[107] but none of these is as effective as chromate or zinc formulations.

The composition and volume of the cooling water blowdown will vary from plant to plant for any given process. Some typical ranges of concentration of contaminants are available, however, from a survey of fertilizer plants in the USA[4]. The volume of blowdown required in an ammonia plant is usually in the range of 1-2% of the cooling water flow. The composition of the waste stream may be typically in the ranges summarized in Table 43.

TABLE 43. - Composition of Ammonia Plant Cooling Water Waste Stream

Contaminant	Concentration, g/m^3	Contaminant	Concentration, g/m^3
Chromate	0-300	Ammonia	10-100
Phosphate	0-50	Monoethanolamine	0-10
Zinc	0-30	Sulphate	500-5000
Heavy Metals	0-60	TDS	200-10 000
Fluoride	0-10	BOD	10-300
Biocides	0-200	COD	15-400
Miscellaneous Organics	0-100	Oil	10-1000
Volume:	1.7-4.2 m^3/tonne of ammonia		

A similar waste stream will be generated in ammonium nitrate production except that there will be a significant nitrate concentration. The blowdown from a urea plant has a volume in the range 0.8-3.4 m^3/tonne of urea. Its composition will again be similar to the ammonia plant blowdown, with the addition of small quantities of urea (up to 50 g/m^3).

Control of Chromates

Two methods are available for reducing the chromate concentration in the waste water. Chromate can be removed by reduction to the trivalent state with sulphur dioxide, followed by precipitation of chromium hydroxide with lime. This creates a solid waste disposal problem and it may therefore be preferable to recover the chromium on an anion exchange resin. Although the capital cost of the equipment is higher than for a chromate destruction system, the recovery of chromate for re-use may make the process more economical. For example, a 1000 tonne/d ammonia plant with a cooling system purged at the rate of 4.0 m^3/tonne of ammonia will lose chromate at the rate of over 30 tonnes/y if the chromate concentration is 25 g/m^3.

Some typical cost data for chromate removal[4] are given in Table 44.

TABLE 44. - Typical Costs of Chromate Removal

Inhibitor System	Initial Concentration, g/m3	Concentration after Treatment, g/m3		Cost, $/1000 gall*
Chromate Only	200-500	CrO_4	0.05	0.70
		Cr	3.0	
Zinc	8-35	CrO_4	0.05	
		Cr	3.0	0.16
Chromate	17-65	Zn	5.0	
Zinc	8-35	CrO_4	0.05	
Chromate	10-15	Cr	3.0	0.13
Phosphate	30-45	Zn	5.0	

*1 US gall = 3.785 x 10^{-3} m^3

Some information on the costs of an American ion exchange process for chromate recovery are also available[108]. The plant reduces the chromate concentration from 20 g/m^3 to 0.1 g/m^3. The cost of treatment in a 1 million gallon/d plant amounts to about $ 0.1/1000 gall compared with $0.2/1000 gall for the same degree of removal by a chromate destruction process.

Boiler Water

Recycle boiler water systems in which steam condensate is used as make-up water can give rise to a contaminated blowdown stream. It is necessary to prevent scale formation on heat transfer surfaces and some form of treatment is required to remove salts of calcium and magnesium. In low pressure boilers sodium carbonate or phosphate may be added to the feed water to precipitate the hardness salts. Often tannins or mixtures of sodium aluminate and tannins are added to coagulate the precipitate and facilitate its removal in the blowdown. Dissolved gases can give rise to corrosion problems. De-aeration may be used to remove dissolved gases, but often chemicals are used. For example, sodium sulphite is used to combine with dissolved oxygen, and sodium hydroxide is used to keep the water alkaline. The blowdown stream can therefore be expected to contain several contaminants, including phosphate, sulphite, suspended solids and sodium hydroxide. External treatment of the feed water is usually necessary, particularly for high pressure boilers where the requirements for high purity water are very stringent. Hardness can be removed by cation exchange but the complete demineralization necessary for high pressure boilers requires a combination of cation and anion exchange so that less common contaminants such as heavy metals, fluorides, phosphates etc. can be removed. External treatment of the feed water reduces the amount of blowdown required.

Of the fertilizer processes under consideration, urea production in particular requires significant quantities of steam (up to 4000 kg/tonne of urea). With treated make-up water 10-20 cycles of concentration can be used[4]. The blowdown volume is very much smaller than cooling water blowdown and is usually in the range 0.08-0.40 m^3/tonne of urea. Some typical ranges for impurity concentrations are shown in Table 45.

TABLE 45. - Composition of Urea Plant Boiler Water Blowdown

Contaminant	Concentration g/m^3	Contaminant	Concentration g/m^3
Phosphate	5-50	Hardness	50-500
Zinc	0-10	Alkalinity	50-700
Heavy Metals	0-10	TDS	500-3500
Sulphite	0-100	Miscellaneous Organics	0-200
Suspended Solids	50-300	EDTA	0-50

Regeneration of ion exchange resins used for demineralization of boiler feed water will give rise to an effluent stream which has a high concentration of dissolved solids, e.g. calcium chloride.

Deep-Well Disposal of Liquid Wastes

Deep-well disposal is a technique in which liquid wastes are injected into porous sedimentary rocks (sandstones, limestones or dolomites) under pressure. The confining strata overlying and underlying the injection area must be relatively impermeable in order to prevent the escape of the injected waste. The method has been used in the USA for many years for the disposal of large volumes of saline water abstracted during oil production. More recently the method has been extended to other industrial wastes, including those arising in the fertilizer industry[4].

In 1971 it was reported that deep-well disposal is being used by a French fertilizer manufacturer to dispose of the aqueous effluent from the manufacture of 1000 tonnes/d of ammonia and ammonium nitrate[109]. The effluent is produced at the rate of 45 m^3/h and contains 7000 g/m^3 of ammonium nitrate and 3000 g/m^3 of chlorides and sulphates. It is injected to a depth of 1850 m under a pressure of 10 kg/cm^2. The total capital cost of the equipment was 1.5 million francs, and it was estimated that the cost of disposal per m^3 of effluent amounts to 0.7 centimes.

There are many possible hazards in deep-well disposal and an exhaustive hydrogeological survey is essential before the method is used. Some geologists think that there is insufficient knowledge about the hydrodynamic behaviour of underground formations containing injected liquors under pressure. Failure of the strata and liberation of liquid could occur undetected at a point remote from the well. It is important that leakage to the surface and contamination of fresh-water aquifers is avoided. Some criteria for the use of this method of waste disposal have been given by Vonhof and van Everdingen[110].

Self-Sustaining Decomposition of Compound Fertilizers

In recent years the demand for more concentrated compound fertilizers has meant an increase in the percentage of ammonium nitrate. This trend has caused compound fertilizers to enter a range of compositions where a new source of hazard has developed. This is deflagration, or self-sustaining decomposition, where ignition in a narrow reaction zone can be propagated through the entire mass without further supply of energy from outside. Unlike a fire, oxygen is not required either for ignition or to sustain the reaction.

A number of accidents have occurred in the storage and shipping of compound fertilizers. The potential danger in these accidents arises from the large quantities of gas which are evolved, up to 50% of the weight of the original fertilizer[111]. Tremendous amounts of poisonous gases can be generated. Eight hours after an accident in Holland in 1963, when 4000 tonnes of fertilizer decomposed, the atmosphere to the leeward side of the storage building contained 200 ppm of nitrogen oxides and 90 ppm of chlorine.

Such serious pollution of the air could be fatal, and a great deal of work has been done to determine the conditions under which deflagration can occur[111,112]. There has been a suggestion that nitrophosphates might be particularly liable to decomposition because of the presence of calcium phosphate[113]. This inert diluent can absorb the liquids produced during decomposition, which might otherwise delay the progress of the burning front. Sufficient knowledge is now available to avoid formulations in which deflagration is possible. Hazards are only likely to occur if there is an error in the manufacture of the fertilizer.

Noise

The limits of the range of intensities of sound between the threshold of audibility and the threshold of pain have a ratio of about $10^{12}:1$. Sound is measured on a logarithmic scale in which this ratio is divided into 120 units or decibels (dB)

At the threshold of audibility sound produces an air pressure of 2×10^{-5} N/m^2. Sounds are measured by comparison with this threshold value, and the ratio is called the sound pressure level, L_p, according to the formula:

$$L_p = 10 \log \frac{P^2}{P_o^2} = 20 \log \frac{P}{P_o}$$

where L_p = sound pressure level, dB

P = sound pressure, N/m^2, caused by source

P_o = threshold of audibility = 2×10^{-5} N/m^2

Sound pressure measurements are subjected to various weightings which take into account the distribution of frequencies in the sound. The A weighting (i.e. the dB(A) value) is universally employed for noise nuisance because it is closest to perception by the human ear.

It is internationally accepted that 85-90 dB(A) is the safe level of noise for continuous exposure for eight hours a day. For every 3 dB increase the acoustic energy is effectively doubled, so that at 93 dB(A) the period of exposure should be reduced to four hours, at 96 dB(A) it should be two hours, and so on. In this way it is possible to define the maximum exposure to which people working close to noisy machinery may be safely submitted.

Sources of noise in a chemical plant include relief valves, bypass valves, flares and compressors. The greatest hazard is experienced by people working on the site. Compressors, for example, can give rise to a noise level greater than 110 dB(A). Ear defenders must be worn by those people who must work near them, even for short periods of time. Noise can also be a nuisance if there are residential areas close to the plant, although the risk of ear damage is very small. Sources of noise which are above ground level, such as flares and prilling tower fans, are most likely to give rise to complaints.

Measurements of the sound level alone seldom provide sufficient information for noise control. Both the sensitivity of the ear and the efficiency of control techniques vary with frequency, and it is therefore important to have some knowledge of the frequency spectrum of the sound. In order to provide this information a frequency analysis is made into ten octave bands whose middle frequencies are 31.5, 63, 125, 250, 500, 1000, 2000, 4000, 8000, 16000 H_z. With the aid of such an analysis the frequency range in which the noise level is dangerously high can be defined. Some examples of noise level measurements close to typical pieces of noisy equipment which are found in chemical process plants are given by Lacey[114].

Detailed solutions to noise problems cannot be given because each plant will have its own specific problems. An analysis of the noise by the type of measurement mentioned in the previous paragraph will enable decisions to be made on the measures needed to reduce the noise and the necessity of providing ear defenders. In general noise can be suppressed by fitting sound absorbers lined with glass wool, by using baffles to suppress noise from moving air streams, by isolating components with special mountings, and by provision of insulated quiet rooms for employees. The cost will depend upon the individual situation but it will be cheaper to include noise suppression in the design of the equipment than to add sound insulation after the equipment has been installed.

THE ENVIRONMENTAL IMPACT OF POLLUTION FROM THE FERTILIZER INDUSTRY

In this section a description is given of the effects of individual pollutants on the environment. Where relevant data are available comparisons are made between the impact of the fertilizer industry and other sources of the same pollutants. In this context both the total quantities emitted and concentrations of pollutants close to the plant are considered. The importance of the geography of the plant situation and the effects of the local climate are stressed.

Air Pollution

The most important air pollutants are:

- oxides of nitrogen
- oxides of sulphur
- fluorides
- ammonia
- particulates

Appreciable quantities of carbon dioxide and water vapour are also discharged to the atmosphere but these substances are relatively harmless. The visual effect of a steam plume is considered by some people to be an objectionable indication of pollution.

In certain circumstances air pollution can have serious effects on property and on plant and animal life in addition to being a potential hazard to human health. As far as toxicity to man is concerned it is not possible to relate specific diseases to specific concentrations of pollutants. Individuals vary enormously in their response to air pollutants. Those suffering from chronic pulmonary disease, such as bronchitis or asthma, will be much more sensitive than healthy persons to the presence of sulphur dioxide, nitrogen dioxide or particulate matter in the atmosphere. Air pollution is seldom a simple problem of a fixed concentration of an individual pollutant and there may be synergistic effects to be taken into account. The combined effect of smoke and sulphur dioxide is well known to be more dangerous than similar concentrations of either pollutant individually. As a general guide the maximum concentrations for continuous exposure, above which harmful effects may be expected, are approximately*:

NO_2, SO_2, fluorides : 5 ppm

NO, NH_3 : 25 ppm

CO_2 : 5000 ppm

<u>Oxides of Nitrogen</u>

Oxides of nitrogen can have biological and phytotoxic effects, and they can be intimately involved in the formation of photochemical smog. Nitrogen dioxide is far more toxic than nitric oxide. It is therefore significant that the tail-gas from a nitric acid plant is likely to contain at least 50% NO_2, in contrast to oxides of nitrogen liberated as a result of combustion where the ratio of $NO:NO_2$ is of the order of 9:1 by volume[115].

The toxic action of NO_2 is primarily irritation of the lower respiratory passages, with pulmonary oedema developing in severe cases. In milder forms of poisoning, symptoms such as nausea, vomiting and vertigo, with cyanosis and methaemoglobinaemia† may be observed. Such severe symptoms are, however, unlikely to be caused by air pollution. The lowest exposure to nitrogen dioxide that affects man is reported to be 3.5 ppm (6.7 mg/m^3) for 1 hour[116]. Damage to vegetation has been reported for 1 hour exposures to 0.5 ppm NO_2.

Concentrations of nitrogen oxides (either as NO or as NO_2) as low as 0.1 ppm can contribute to the formation of photochemical smog, a very unpleasant form of pollution which is frequently experienced in the USA. This type of smog is much less likely to occur under the meteorological conditions which prevail in Western Europe. Nevertheless there is evidence that photochemical reactions between olefins (from vehicle exhausts) and ozone have occurred in Britain[117].

The major source of oxides of nitrogen in the fertilizer industry is nitric acid manufacture, with emission rates of up to 20 kg/tonne of product, expressed as

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*A more precise definition of harmful concentrations of air pollutants can be found in threshold limit values (TLV's) recommended by the American Conference of Governmental Industrial Hygienists. The TLV is the concentration that can be inhaled for an 8 hour day, 5 day week without adverse effect.

†The formation of methaemoglobin in the blood, which inhibits its capacity to carry oxygen.

NO_2. In comparison emissions from nitrophosphate processes normally amount to less than 0.5 kg/tonne of product. The contribution of nitric acid manufacture to air pollution by oxides of nitrogen is shown in Table 46. In this table the available statistics for nitric acid production in EEC countries in 1970[118], and the estimated total nitric acid capacity in the UK are summarized. The estimated emission from nitric plants was calculated using an average emission factor of 10 kg NO_2/tonne of nitric acid[16,43]. These figures are compared with total NO_x emissions from all sources (including traffic domestic heating and power stations) where data are available. In Germany and the UK it can be seen that 1-2% of the total NO_x emissions come from nitric acid manufacture. In Germany 80% of the nitric acid production is used by the fertilizer industry. The overall contribution of nitric acid manufacture to pollution by oxides of nitrogen is therefore relatively small and it is basically a local problem restricted to a small number of production centres.

TABLE 46. - The Contribution of Nitric Acid Manufacture to Air Pollution by Oxides of Nitrogen

Country	1970 HNO_3 Production million tonnes	Estimated NO_x emission at 10^xkg/tonne HNO_3 thousand tonnes	Total NO_x emission from all sources million tonnes	Reference
Belgium	0.7	7	-	-
France	2.6	26	0.9	119
W. Germany	3.3	33	2.00	120
Italy	1.0	10	-	-
UK	2.0*	20	1.46	115

*Estimated capacity

The data quoted in Table 47 give some interesting information on the order of magnitude of concentrations of oxides of nitrogen which have been measured in the vicinity of nitric acid plants[13]. The radius of the polluted zone around the factory and the average concentration (calculated as NO_2) tended to increase with production capacity. Both the average and maximum concentration of the polluted zone around the plants with high stacks were well below the concentration of around 7 mg/m^3 above which affects on man can be observed. This is not true of the plant which had several low chimneys, where a maximum concentration of 2.1 mg/m^3 was measured. In a survey of nitrogen oxide concentrations near sources of pollution in the UK[115] the highest concentrations were registered in Fleet Street, London. The concentrations reported were

TABLE 47. - Nitrogen Oxide Emissions from Nitric Acid Plants in Germany*

Plant	Daily HNO_3 production, (tonnes)	Volume of NO_2 per day, (m^3)	Daily HNO_3 loss, (tonnes)	Stack Height, (m)	Radius of polluted zone, (km)	Average NO_2 conc. in zone, (mg/m^3)	Maximum NO_2 conc. in zone, (mg/m^3)
1	360	3000	5.7	75	2	0.013	0.61
2	480	4300	8	108	2	0.017	0.08
3	600	5400	10.2	100	6	0.017	0.23
4	600	-	-	-	3	0.026	0.28
5	-	-	-	10-70 (several chimneys)	4	0.100	2.1

*The concentration of NO_x emitted from the plants was in the range 2000-3000 ppm ($4000-6000\ mg/m^3$)

1.0 mg/m^3 NO and 0.2 mg/m^3 NO_2, concentrations at most other urban sites being an order of magnitude lower. The maximum concentrations quoted in Table 47 are of the same order of magnitude, and bearing in mind the greater proportion of the more toxic NO_2 in nitric acid plant emissions, the pollution by oxides of nitrogen in the vicinity of the plants was therefore equivalent to the pollution from traffic in a busy city centre street. Although it is dangerous to generalize from limited data, these results do suggest that, even where a high stack is used to disperse the emissions, the pollution in the vicinity of the plant from many existing nitric acid plants could reach a level close to that caused by traffic in a city centre. Much will depend on the geographical situation of the plant and the local climate. The pollution would be more serious in a situation where atmospheric inversions are common.

Oxides of Sulphur

The effects of sulphur dioxide at low concentrations have been studied extensively in connection with its presence in polluted atmospheres. Concentrations in excess of 10 ppm (26.6 mg/m^3) are strongly irritating and some irritation occurs at 5 ppm, which is generally recognized as the maximum safe concentration for continuous exposure. The harmful effect of sulphur dioxide is accentuated by the presence of particulate matter, symptoms being most likely in people suffering from chronic bronchitis. The concentration of sulphur dioxide in severe pollution episodes, such as have been experienced in London smogs, seldom exceeds 1-2 ppm. Normal pollution levels are usually less than 0.1 ppm.

Plants are much more sensitive to sulphur dioxide than man. They vary in susceptibility but injury to the most sensitive species can occur at concentrations as low as 0.15 ppm. Other factors, such as temperature, humidity, light intensity and nutrition can modify the effects. Sulphur is a nutrient in growing crops and provided that the concentration of sulphur dioxide in the atmosphere is kept sufficiently low its presence may be beneficial. This is particularly true as the trend away from sulphur-containing fertilizers continues. It has been calculated that the present emissions of sulphur dioxide in the USA, if evenly distributed, would make up for sulphur deficiencies in the soil[121]. The problem is entirely one of distribution.

The lifetime of sulphur dioxide in the atmosphere is probably only a few days. It is removed by direct absorption by vegetation, soil or water, and by chemical reactions in the atmosphere. In the presence of sunlight oxidation to sulphur trioxide can occur, leading to the formation of sulphuric acid aerosol. If ammonia is also present there is evidence for the formation of ammonium sulphate aerosol[122].

In addition to its formation by chemical reactions in the atmosphere, sulphuric acid mist may be emitted directly from a sulphuric acid plant. The most obvious effect will be the appearance of a dense white plume. Not surprisingly sulphuric acid mist can act as a bronchial irritant, giving rise to symptoms in concentrations above

0.1 ppm (0.4 mg/m^3). Concentrations of this order of magnitude have been observed in London smogs[123].

The atmosphere around a sulphuric acid plant will therefore contain a complex mixture of pollutants, including sulphur dioxide, sulphuric acid and, in the presence of ammonia, ammonium sulphate aerosol. In addition to adverse health effects all of these pollutants may be effective in promoting corrosion.

Total emissions of sulphur dioxide from the manufacture of sulphuric acid in EEC countries are estimated in Table 48. Production figures and the fraction used in fertilizer manufacture[124] are summarized in the Table.

TABLE 48. - The Contribution of Sulphuric Acid Manufacture to Air Pollution by Sulphur Dioxide

Country	1970 H_2SO_4 Production, thousand tonnes	H_2SO_4 used in Fertilizers, %	Estimated SO_2 Emission at 13 kg/tonne H_2SO_4 thousand tonnes	Total SO_2 from all sources, million tonnes	Reference
Belgium	1949	58	25.3	-	-
Denmark	240	91	3.1	-	-
France	3596	61	46.7	2.2	119
W Germany	4435	28	57.7	4.0	120
Italy	3319	46	19.8	-	-
Netherlands	1563	45	20.3	-	-
UK	3352	35	43.6	5.95	125

The quantities of SO_2 emitted in each country are based upon the total acid produced and it is assumed that all acid is manufactured in conventional contact plants with an efficiency of 98%. The corresponding emission factor is 13 kg/tonne of sulphuric acid. Sulphur dioxide from sulphuric acid manufacture amounts to 2.3% of the total in France, 1.4% in Germany and 0.7% in the UK.

Published measurements of concentrations of air pollutants close to a sulphuric acid plant are scarce. An average SO_2 concentration of 5 ppm was measured around a plant in Egypt[126]. The plant produced around 80 tonne/d of sulphuric acid and had a 20 m stack. Concentrations of acid mist emitted from two 50 m stacks at a plant in California[127] varied between 0.003 mg/m^3 and 0.03 mg/m^3. These concentrations are below the level at which bronchial irritation can be expected but the sulphur dioxide concentrations measured at the Egyptian plant are higher than is desirable. The usual caveat about the location of the plant and meteorological conditions applies. Nevertheless similar conclusions to those applying to nitric acid manufacture can be drawn. The overall contribution of the industry to the total air pollution in a country is relatively small, but concentrations of air pollutants in the atmosphere near the plant may reach undesirably high levels.

Fluorides

In addition to the phosphate fertilizer industry other sources of fluorine compounds in the atmosphere include aluminium production, steel making, the brick, tile and ceramic industries and the burning of industrial and domestic coal. Of these sources, all but the last are localized sources restricted to a few, highly polluted areas. There has been a long history of damage to the environment caused by fluoride emissions from these industries. Two major air pollution disasters have been ascribed to the presence of high fluoride concentrations in the atmosphere, although other noxious gases were undoubtedly also present. The first of these disasters happened in December 1930 in the Meuse Valley of Belgium during a period of fog and thermal inversion. Several thousand people became ill and sixty deaths occurred. A Commission of Investigation was unable to name any definite chemical compounds as the cause of the disaster but suggested sulphur dioxide as the most likely culprit. Later, however convincing evidence was presented by Roholm[128] that acute intoxication by gaseous fluorides was responsible. In 1948 a similar incident was experienced in Donora, Pennsylvania. Again fluorine in conjunction with other chemical agents was responsible. Apart from these two major disasters the available evidence suggests that the damage caused by fluorides in the atmosphere to vegetation and animals is much greater than the ill effects on man.

The acute effects of increasing concentrations of gaseous fluorides can be listed as follows:

3 ppm (2.4 mg/m^3) - no immediate effects
10 ppm (8 mg/m^3) - many persons experience discomfort
30 ppm (24 mg/m^3) - all persons complain and object to staying in environment
60 ppm (48 mg/m^3) - Brief exposures cause irritation of eyes, nose, pharynx, upper chest
120 ppm (96 mg/m^3) - not tolerable for more than 1 min, all above effects intensified, smarting of skin

The first sign of chronic fluorosis is mottling of the teeth. Further symptoms include pains and stiffness in joints. Radiological examination of workers exhibiting these symptoms has shown evidence of bone-thickening and ossification of the ligaments (osteosclerosis). A survey of the literature describing the exposure of workers to fluorides in industrial atmospheres indicated that concentrations were mostly less than 10 mg/m^3 [129]. Although there were occasional complaints of the irritating symptoms listed above, and radiography showed evidence of mild osteosclerosis in some individuals, only a few instances of crippling fluorosis have been authenticated. These cases were caused by working in conditions that would be completely unacceptable at the present time. The daily fluoride intake at a concentration of 2.5 mg F/m^3* was calculated to be 5-6 mg, while the maximum daily intake that will never induce detectable osteosclerosis was estimated to be 5-8 mg. Muscular pains, gastro-intestinal and respiratory symptoms, as well as skin lesions have been described in patients residing near fertilizer factories in the USA and Canada[130]. These individuals were suffering from fluorosis in the pre-skeletal phase.

In addition to the toxic effects of fluoride, inhalation of silicon tetrafluoride can lead to the deposition of silica in the lungs. Respiratory ailments are said to be common amongst the inhabitants of the part of Florida where large quantities of phosphate rock are processed[130].

There is a long history of injury to vegetation caused by industrial emissions of fluorides, and there have been many successful claims for damages against the responsible firms[131]. Fluorides appear to act as cumulative poisons, entering the leaves and causing a characteristic tip and marginal scorch. The susceptibility of different species varies over two to three orders of magnitude. The most sensitive plants are those which absorb the gas rapidly e.g. gladioli, peach, tulip and young pine needles. As little as 15-40 μg/m^3 of fluoride will damage gladioli and certain fruit trees. In Florida some 100 km^2 of citrus plantation have been destroyed by fluoride emissions from phosphate rock processing[130]. Damage on this scale is not experienced in Europe but it is a real and continuing problem in spite of control measures used in modern plants. A European fertilizer manufacturer employing efficient scrubbing equipment admits that serious damage is caused to vegetation near the factory.

Fluorine concentrations in contaminated plants can build up to very high levels. Some measurements near a fertilizer factory in Germany[132] yielded fluorine concentrations as high as 1850 ppm (by weight) in plants 500 m from the factory in the direction of the prevailing winds. In the opposite direction an average concentration of 200 ppm was found. Normal average concentrations in uncontaminated plants would be 7-15 ppm. High concentrations of fluoride in rain water were also measured in the same area.

High fluoride concentrations in forage crops can induce fluorosis in livestock. Concentrations in excess of 30 ppm are toxic to cattle. Plants may also be contaminated with insoluble fluoride-containing dusts but this is thought to have little effect on plants or animals. A further, and disturbing effect of fluoride contamination is the biosynthesis of fluoroacetate and fluorocitrate[133]. These compounds are extremely toxic to animals and may cause ill effects additional to those due to inorganic fluorides.

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*This is the threshold limit value (TLV).

Some estimates of fluoride emissions to the atmosphere are given in Table 49. The gaseous fluoride emissions for the fertilizer industry are based upon the following assumptions:

Phosphoric acid - 0.1 kg F/tonne P_2O_5
Superphosphates - 1.0 kg F/tonne P_2O_5
NPK Compounds via Ammonium Phosphate - 0.1 kg F/tonne P_2O_5
Nitrophosphates

For the purposes of the calculation it was also assumed that compound fertilizers were made by the nitrophosphate route in Germany and Holland. The source of the statistics upon which the figures in Table 49 are based has requested that the individual country production figures should not be disclosed. Therefore only the calculated total fluoride emissions from all the processes considered are quoted in the Table. Estimates of fluoride emissions from other sources are not available for most countries but in 1961 it was estimated that 25 000 tonnes of fluorine were emitted annually in England and Wales[134]. Twelve thousand tonnes were derived from the industrial use of fluorspar (of which 10 000 were emitted in the manufacture of steel), 5000 tonnes from the industrial and domestic use of coal, 4500 tonnes from the heavy clay industry, 600 tonnes from the treatment of iron ores, 500 tonnes from the cement industry and 150 tonnes from the pottery industry. Although the relative emissions from different industries will have changed since 1960 and will vary from country to country, It would appear that the contribution of the fertilizer industry to the total emission of fluorides is quite small.

TABLE 49. - Estimated Fluoride Emissions to the Atmosphere in 1971 from Fertilizer Manufacture

Country	Fluoride Emissions, tonnes F
Belgium	160
Denmark	80
France	580
W Germany	70
Ireland	80
Italy	270
Netherlands	160
UK	160

Table 49 reveals some interesting features. A relatively high proportion of superphosphates is still manufactured in France and Italy, and this is the reason for the relatively high fluoride emissions from the fertilizer industry in these countries. The lowest fluoride emissions come from the German fertilizer industry where superphosphates are less important and the production of compound fertilizers is mainly by the nitrophosphate route.

It is estimated that the total consumption of phosphate rock in the fertilizer industry in EEC countries in 1971 was around 12 m tonnes. Assuming that the fluorine content was 3% and that one third of this was released as gaseous fluorides during processing, a total of 120 000 tonnes of fluorine was released in 1971. The total fluorine released to the atmosphere, according to the data in Table 49, amounted to 1560 tonnes, which implies an average scrubbing efficiency of 98.7%. This is a reasonable value and lends support to the reliability of the data in the table. Most of the 120 000 tonnes of released fluorine will have been discharged as an aqueous effluent.

From the limited amount of information available it appears that fluoride concentrations up to 30 $\mu g/m^3$ have been measured in the vicinity of superphosphate plants[61,135]. The concentration was highest in the direction of the prevailing winds and there was evidence of damage to vegetation. In a survey of fluoride concentrations in the ambient air in the USA it was concluded that few samples contained more than 1.0 $\mu g/m^3$ of fluoride[136]. Although it is not surprising that vegetation near a fertilizer factory is injured, the measured concentrations of fluoride are well below the levels at which harmful effects on man can be expected. It should also be pointed out that accurate measurement of fluoride concentrations is very difficult.

Ammonia

Due to its alkaline properties ammonia is irritating to the mucous membranes of the nose, throat and eyes and, in high concentrations, to the skin. Mild irritation to the throat is observed at 50 ppm (35 mg/m^3) but severe effects require several hundred parts per million. The odour threshold for ammonia is 50 ppm.

The available data do not permit a calculation of ammonia losses to the atmosphere from fertilizer processes but some relevant estimates have been made for the UK[122]. The ammonia concentration in the atmosphere over the UK is fairly constant at about 4 $\mu g/m^3$ of ammonia + ammonium ion. This indicates a widespread source, probably the urea in animal urine, which may contribute about 75 000 tonne/y of ammonia to the atmosphere. The chemical industry probably contributes no more than about 2000 tonne/y. Locally, however, the burden from industry may be significant. Ammonia concentrations in the atmosphere at Billingham have been steadily reduced from 60 $\mu g/m^3$ in 1967 to less than 20 $\mu g/m^3$ in 1971[137].

Ammonia emissions per se are unlikely to exert any harmful effects. There is, however, a secondary effect which can be a considerable nuisance. It has been shown that, in the presence of ammonia, the main oxidation product of sulphur dioxide in the atmosphere is ammonium sulphate aerosol[117,122]. In coastal situations like Billingham, where advection inversions give rise to stable fogs, pollution from moderately high stacks can be trapped and brought down to ground level. The presence of ammonium sulphate considerably increases the density and unpleasantness of the fog. Fogs at Billingham have been alleviated since 1970 with the 97% reduction of sulphur dioxide emissions which has been obtained as a result of the change to natural gas as a fuel.

Particulates

Most of the particulate emissions from fertilizer manufacture will consist of water soluble plant nutrients, mainly as a result of emissions from prilling towers. Because of the more favourable economics of wet scrubbing in granulation plants, dust emissions will in general be much lower than from prilling towers, although in those plants in which the only control measure is a battery of dry cyclones there will be significant emissions of fine dust. The overall contribution of granulation plants to the total dust burden is, however, not known.

In making an estimate of the total particulate emissions from the fertilizer industry only those products which are normally produced in a prilled form, (i.e. ammonium nitrate, calcium ammonium nitrate, urea) have been included in the calculation. An emission rate of 2 kg dust/tonne of product has been assumed. The results are shown in Table 50. As with the other atmospheric pollutants, it is clear that the fertilizer industry's contribution to overall particulate emissions is relatively small.

TABLE 50. - Estimated Particulate Emissions from Prilling Towers

Country	Particulates from Prilling Towers, thousand tonnes	Total Particulates, million tonnes	Reference
Belgium	1.4	-	-
Denmark	0.2	-	-
France	4.8	1.1	119
W Germany	3.8	4.0	120
Ireland	0.3	-	-
Italy	2.7	-	-
Netherlands	3.4	-	-
UK	3.2	0.8*	125

*smoke from coal combustion only

There is very little available information on the effect of these emissions on the environment. An estimate of the probable effect of a plant producing 600 tonne/d of ammonium nitrate prills was made before the plant came into operation. The plant was designed to emit a maximum of 500 tonnes of ammonium nitrate dust annually. Most of this dust was expected to fall in an area within about 1 km of the plant at a rate of around 200 g per m^2 per year. This is equivalent to a daily rate of dustfall amounting to one sixtieth of a typical single application by a farmer in the normal use of a fertilizer. In the vicinity of the plant the effect on vegetation was predicted to be generally beneficial. In practice the prevailing winds tend to concentrate the dust into a small sector so that sufficient fertilizer is deposited on vegetation to cause scorching. Once again the prevailing meteorological conditions are seen to be of the utmost importance in determining the amount of damage caused by air pollution.

Water Pollution[4]

Aqueous effluents from fertilizer plants, in common with those from other industries, can have three basic effects upon the environment:

(a) Most important is the possibility of causing biological or physiological changes in organisms in the receiving water or those using the water. Serious interference with the ecological balance in the aqueous environment can occur. Effects on aquatic plant life must be expected because a large proportion of the waste from a fertilizer factory will consist of plant nutrients.

(b) They can affect renovation or re-use of the receiving water. The presence of toxic materials can seriously interfere with the subsequent use of the receiving waters for public water supplies, animal life and irrigation. Dissolved materials can cause corrosion problems, scaling, and undesired side reactions in water used for industrial purposes.

(c) They can affect the aesthetic or recreational value of the receiving water. This is difficult to define quantitatively but the effects of uncontrolled waste discharge are well known. Floating material, oil slicks, scum, turbidity, colour, odour, excessive plant growth all serve to detract from the beauty of lakes and rivers.

Parameters for Evaluating Aqueous Effluents

Water pollution from the fertilizer industry must be considered in terms of the conventional pollution parameters, such as temperature, pH, oxygen demand etc., as well as those contaminants, mainly inorganic ions, which may individually have an adverse effect on the environment. The following list of factors is considered to be important in evaluating the effects of water pollution from the fertilizer industry.

Conventional Pollution Parameters

pH
Biochemical Oxygen Demand (BOD)
Chemical Oxygen Demand (COD)
Dissolved Oxygen (DO)
Total Dissolved Solids (TDS)
Suspended Solids
Temperature

Major Inorganic Contaminants

Phosphate
Ammonia
Nitrate
Fluoride
Sulphate

Minor Inorganic Contaminants

Chromate
Heavy Metals

Organic Contaminants

Urea
Lubricating Oils

In classifying water pollution in this way it must be remembered that there is a continuous interplay between the various parameters under discussion. For example, a change in temperature will have an effect on the oxygen demand and dissolved oxygen in the water, as well as possible effects on the toxicity of any contaminants which are present.

Conventional Pollution Parameters

Most natural fresh waters have a pH value close to 8 and aquatic life, both animal and plant, exists most effectively in water that is near this value. Most aquatic life can tolerate a pH range from 5-9 without serious consequences.

Biochemical oxygen demand (BOD) is defined as the oxygen required for oxidation of soluble organic matter by bacterial action in the presence of oxygen. The test is carried out under standardized conditions of temperature (20°C), time (5 days), dilution, pH etc. BOD is a measure of biodegradable organics present in a waste stream.

If the BOD of the receiving water is raised excessively the result can be a reduction in the dissolved oxygen in the water to a point where aquatic life suffers damage. Chemical oxygen demand (COD) is the amount of oxygen consumed by an organic waste from a chemical oxidizing agent. It does not distinguish biodegradable materials from those that are non-biodegradable but it has the advantage of yielding a value in much less than 5 days.

Oxygen demand is a less important criterion of pollution in waste water from the fertilizer industry than it is for many other branches of the chemical industry because the contaminants present are mainly inorganic materials, Nevertheless, waste streams containing urea and ammonia can exert an oxygen demand.

Oxygen is required to sustain aquatic life. The solubility of oxygen in water ranges from 11.3 g/m^3 at 10^oC to 5.6 g/m^3 at 50^oC. In cold water fresh water organisms require at least 6 g/m^3 for good growth, and in the UK the Royal Commission on Sewage Disposal has suggested that a river is on the verge of becoming unpleasant if the dissolved oxygen concentration falls below 5-7 g/m^3. In addition to direct effects on aquatic life, a reduction in dissolved oxygen reduces the threshold concentration of substances toxic to fish.

Total dissolved solids is essentially a measure of the dissolved inorganic materials in a water sample, principally mineral salts. High concentrations of dissolved solids can impart a mineral taste to drinking water and possibly produce physiological effects in humans and animals. The maximum dissolved solids concentration recommended by the World Health Organization (WHO) for drinking water is 1500 g/m^3. This limit assumes that the individual dissolved solids are relatively non-toxic and are harmful only at high concentrations where their osmotic effect in organisms becomes excessive. High dissolved solids can also cause corrosion of metals and materials of construction. They can cause scaling problems in cooling water systems, increasing the necessity for purging, and thus increasing the contribution of cooling water and steam generation systems to the overall water pollution problem.

High suspended solids, or turbidity, in a waste stream can have a number of harmful effects on the receiving waters. It can reduce the light reaching aquatic plant growth, thus reducing photosynthesis. Its effect after settling on flora and fauna on the river or lake bottom may be catastrophic, so that, even if fish survive in a relatively clean supernate, they have very little to eat and cannot thrive. Concentrations of suspended solids above 100 g/m^3 are unlikely to support good fish growth, while very high concentrations may directly kill fish by blocking their gills.

Thermal pollution, arising principally as a consequence of the discharge of cooling water, can be a serious problem. The oxygen content of water can be reduced by increasing temperature, either directly as a result of the reduced solubility of oxygen or indirectly as a result of an increase in the rate of the chemical and biochemical reactions which occur in the water. In addition the toxicity of poisonous chemicals may be increased.

Inorganic Contaminants

Estimates of the total water pollution load from the manufacture of fertilizers, similar to those made for air pollution, would be difficult to make on the basis of the information that is available and probably not very reliable. There are a number of reasons why this is so. There are wide variations in the processes for the manufacture of compound and complex fertilizers, and without detailed information on the composition of the waste streams produced by different manufacturers, definition of a "typical effluent" is not possible. Fertilizer dusts, which are primarily an air pollution problem, will dissolve in rain water after settling on the ground and contribute to the water pollution burden. Soluble gases which are present in the atmosphere, such as ammonia and sulphur dioxide, will dissolve in the water which is passing through cooling towers. Lastly, there may be a considerable contribution to the overall water pollution problem from process leaks and spills. All these contributions are difficult to estimate quantitatively and any generalization would be unreliable.

Although a quantitative estimate cannot be made, it seems likely that the contribution of the fertilizer industry to the total water pollution burden due to the primary nutrients, (i.e. nitrogen and phosphates) is quite small relative to the contribution from sewage and agricultural run-off. As was the case with air pollution, however, serious environmental deterioration may occur near the individual factories. The effects of individual contaminants on the water into which they are discharged are now considered in detail.

Phosphate

The presence of low phosphate concentrations in water can lead to rapid growth of algae and other vegetation. Concentrations of phosphorus as low as 0.01 g/m^3 are sufficient for the growth of algal blooms. Phosphate in water courses can therefore contribute to the excessive aquatic plant growth which leads to eutrophication. Most of the increased phosphate levels in rivers in developed countries can be attributed to sewage effluents, and in particular to detergents.

Apart from the possibility of contributing to eutrophication, phosphate in water is relatively harmless. Concentrations of up to 100 g/m^3 are tolerable in public water supplies. Phosphates can cause scaling problems in water used for steam generation and cooling purposes.

Ammonia

Ammoniacal nitrogen is assimilated more rapidly by plant life than any other form of nitrogen. Although ammonium compounds are converted into nitrates by nitrifying bacteria in water, they may in themselves contribute to eutrophication. Because of the bacterial oxidation in water, dissolved ammonia can exert an oxygen demand. For every gram of ammoniacal nitrogen oxidized, 4.57 g of oxygen are required.

Ammonia in water can be toxic to fish at concentrations of 2-3 g/m^3. The pH has an important effect on ammonia toxicity, which depends primarily on non-ionic ammonia and undissociated ammonium hydroxide. When the pH is greater than 8 the ammonia concentration, as nitrogen, should not exceed 1.5 g/m^3.

When water is disinfected with chlorine, a common procedure in water used for cooling, any ammonia present in the water will react to form chloramines. The chloramines are less effective as bacteriocides than chlorine, and are toxic to fish at concentrations as low as 0.4 g/m^3. The presence of ammonia in water used for drinking water supply can upset the chlorination facilities at water treatment works.

Ammonia can be quite corrosive to certain metals, particularly copper and zinc alloys. Ammonium salts also attack concrete made from Portland cement.

Nitrate

Nitrate ion is also a potential cause of eutrophication. It appears that the nitrate level (<10 g/m^3) in rivers in rural districts arises mainly as a result of land drainage. In urban districts, particularly close to sewage works, higher concentrations, (>20 g/m^3) are common. Waste water from industrial processes is also likely to be an important contributor in receiving water close to the plant. Algal development can readily occur in water containing less than 1 g/m^3 of nitrate-N.

Nitrate ion can be toxic to humans and animals. In humans the risk is confined to babies, who can suffer methaemoglobinaemia caused by microbial reduction of nitrate to nitrite and the subsequent absorption of nitrite in the blood. Nitrate concentrations in drinking water exceeding 70 g/m^3 are dangerous to babies, and such high concentrations have been known to occur in water obtained from deep wells. The WHO limit for potable waters is 22.6 g/m^3 nitrate nitrogen, with a recommendation that Medical Officers of Health should be notified when the nitrate content of water supplies exceeds 50% of this figure. Nitrates can also cause methaemoglobinaemia in cattle and pigs, but high concentrations, (>1000 g/m^3) are required.

Fluoride

Soluble fluorides are toxic to animal and plant life, and their effects have already been discussed with reference to air pollution. Continuous ingestion of drinking water containing 2-3 g/m^3 of fluoride causes mottled teeth, while higher concentrations can cause severe fluorosis. Deaths have been reported from the continuous ıse of water containing 13 g/m^3 fluoride. The WHO recommends a maximum concentration of 1.5 g/m^3 in drinking water, which is remarkably close to the concentration of 1.0 g/m^3 recommended for the fluoridation of water supplies. The balance between beneficial and toxic effects due to fluorides in drinking water is very complex, and it is discussed in detail in a WHO monograph[134]. Aquatic plant life does not appear to be adversely affected by concentrations of fluorides of less than 50 g/m^3, so higher concentrations than 1.5 g/m^3 are tolerable in water not used as drinking water.

Sulphate

Sulphate ion in water is not considered to be toxic in moderate amounts, though high concentrations in drinking water can have a laxative effect. The WHO recommended maximum concentration is 400 g/m^3. Sulphate ion in industrial water can be a potential cause of scaling. High sulphate in recycled boiler or cooling water therefore increases the necessity for purging and creates a larger waste stream. Sulphate concentrations higher than 1000 g/m^3 can cause damage to good-quality concrete.

Chromium and Heavy Metals

Chromium in the hexavalent state (CrO_4^{2-}, $Cr_2O_7^{2-}$) is extremely toxic to plant and animal life. Continuous ingestion of chromates can cause intestinal inflammation, kidney damage and lung cancer. Chromate concentrations greater than 0.2 g/m^3 are toxic to algae and other aquatic plant life, and concentrations greater than 1 g/m^3 are toxic to many species of fish. The WHO maximum allowable concentration in drinking water is 0.05 g/m^3.

The heavy metals as a group are also extremely toxic, although zinc, which is the one most likely to be found in waste water from fertilizer manufacture is one of the least toxic of the group. The WHO recommends a maximum concentration of 15 g/m^3 for zinc.

Organic Contaminants

Urea

Urea is used as an animal food supplement and is not considered to be toxic to animal life. It is a normal product of metabolism and is excreted in fairly large quantities. Systematic administration of doses of 1000 g/m^3 does not disturb the urea balance in the body[138]. It can, however, impart a taste to water at a concentration of 10 g/m^3.

Although urea readily undergoes biochemical decomposition it does not disturb the BOD of water courses at concentrations up to 500 g/m^3 [138]. This is because the first stage of oxidation to ammonium carbonate in the presence of the enzyme urease, does not require the participation of the oxygen dissolved in the water. Subsequent decomposition produces ammonia, which can undergo nitrification in the normal way, thus exerting an oxygen demand. The complete oxidation of 1 mg urea would require about 2 mg oxygen. Only minimal hydrolysis of urea is likely to occur in river water. It has been shown that standard waterworks chemical treatment processes have very little effect on urea[139]. Any urea in river water used for domestic supplies would pass virtually unaltered into the drinking water.

Urea is a plant nutrient but assimilation by plants is slow relative to ammoniacal or nitrate nitrogen. It is doubtful whether urea contributes significantly to eutrophication.

Lubricating Oils

Oil in waste streams can lead to a number of adverse effects. It can coat the water with a thin film and reduce the aesthetic value of the water. The presence of the film interferes with dissolution of oxygen in the water, thus adding to all the problems which are created by a shortage of dissolved oxygen. A coating of oil on waterfowl, fish and aquatic plant life can have serious effects. In addition components of the oil may be toxic to aquatic life. The presence of oil in public water supplies can create an odour and taste problem. Water authorities in the UK usually require a concentration of oil of less than 10 g/m^3 as a condition for consent for the discharge of industrial effluents.

Summary

The total quantities of pollutants discharged to the atmosphere from the fertilizer industry are small relative to other sources. The dispersion and concentration of pollutants in the air in the locality of the plant is of primary importance in assessing whether any ill-effects may be caused to life in the neighbourhood of the plant. There are, however, few published measurements of concentrations of pollutants which can be attributed to fertilizer processes. It is often difficult to determine the effect of individual sources of emission because of the vicinity of other sources of pollution. An example is provided by measurements made near a fertilizer complex in Canada[140]. The monthly variations in the concentrations of fluoride and sulphur dioxide in the atmosphere were closely parallel, indicating a common source for these two species. It was concluded that the fluoride and sulphur dioxide originated in the combustion of coal in a nearby power station, and it was not possible to make any measurements of fluoride concentrations which could be attributed to the operation of the fertilizer processes.

The available results indicate that there is widespread damage to plants in the neighbourhood of some fertilizer factories. Plants are particularly susceptible to fluorides, which are probably the most important cause of damage, though scorching due to the deposition of fertilizer dust may also occur. Some ill effects can be expected in animals grazing on contaminated vegetation, but emissions from fertilizer manufacture can be expected normally to have little effect on healthy humans. Nevertheless, concentrations have been observed of pollutants quite close to the threshold concentrations above which detectable effects on man can be expected. In normal weather conditions there may be no hazard, but in certain geographical locations dangerous concentrations may build up in the atmosphere when there is an inversion. Such incidents are very rare but in protecting the community against possible harm from pollution, the worst possible event that can happen must be taken into account. The local topography and climate are very important and calculations of dispersion of plumes from chimneys in idealized conditions may be invalid. These considerations raise doubts about claims that the consequences of some types of air pollution may be beneficial. The use of modern air pollution control techniques increases the safety margin so that even in abnormal weather conditions the public is protected against harmful effects from atmospheric pollution.

The greatest water pollution problem arising from the operation of the fertilizer processes which have been discussed is the discharge of plant nutrients to receiving waters. With exception of fluoride the contaminants in waste streams from fertilizer processes are not highly toxic, and oxygen demand is a much less important problem than in many other sectors of the chemical industry. The concentrations of contaminants in the various process waste streams are frequently high enough to adversely affect aquatic life, and they may raise problems if discharged into water which is used as a source of drinking water.

SUMMARY OF THE ECONOMICS OF POLLUTION CONTROL AND GENERAL CONCLUSIONS

Air Pollution

In Europe it is probably true to say that most of the expenditure on pollution control in the fertilizer industry is devoted to the control of air pollution. On many sites local, rather than national, regulations must be obeyed, and this has led to some companies building plants to higher emission standards than demanded by national laws. For the purpose of examining the effect of legislation on the cost of air pollution control, UK regulations have been chosen as typical of the standards which can be met with available technology at reasonable cost. In Table 51 estimates of the costs incurred in meeting these standards are compared with the estimated costs of meeting the more stringent standards which have been proposed in the USA. It has not been possible in many cases to obtain cost data for a range of plant capacities, because contractors and manufacturers prefer to quote costs only for building plants in a capacity range of which they have had recent experience.

TABLE 51. - Estimates of Cost of Meeting Air Pollution Regulations for New Plants in UK and USA

Process	UK			USA		
	Emission Standard	Plant Capacity, tonne/d	Cost, $/tonne	Emission Standard	Plant Capacity, tonne/d	Cost, $/tonne
Nitric Acid						
Extended Absorption	7 kg NO_2/tonne HNO_3 (1000 ppm)	500	0.51-0.65	1.5 kg NO_2/tonne HNO_3 (200 ppm)	300 550 600	1.04 1.17 0.35
Catalytic Reduction		-	-		300 500	1.23 0.94
Molecular Sieve					300	1.74
Sulphuric Acid						
Double Contact	3 kg SO_2/tonne H_2SO_4 (99.5% efficiency)	700-1000	0.42	2 kg SO_2/tonne H_2SO_4	230 680 1350	0.45 0.20 0.13
Tail Gas Treatment		-	-		230 1350	2.75 0.80
Molecular Sieve		-	-		180	2.23
Phosphoric Acid	F conc. <320 mg/m^3 or washing efficiency >99%	180	0.5	0.01 kgF/tonne P_2O_5	450 800	0.15-0.25 0.10-0.17
TSP						
Granular by TVA Process	F conc. <320 mg/m^3 or washing efficiency >99%	-	-	0.10 kgF/tonne P_2O_5	230 360	5.53 5.10
Den		720	~0.50		-	-
Granulated NP and NPK fertilizers	Dust 0.46 g/m^3 Acidity 0.46 g/m^3 as SO_3	600 600 with two abatement scrubbers	<0.25 0.90	0.03 kgF/tonne P_2O_5	1000 1600	0.38 0.29

There seems to be little doubt that the best method of achieving the standard currently set in the UK for nitric acid plants is by the provision of increased absorption capacity. The increased production cost is about $0.5 per tonne of nitric acid in a 500 tonne/d plant, which is representative of the size of recently built plants. The American standard for new plants can be met at a cost which is approximately twice as high by means of a mixed-pressure process, although there is one mono-pressure process which is said to achieve the same standard at a very much lower cost. Catalytic reduction can also achieve the same standards at a cost of around $1.0/tonne, possibly less in plants fitted with a high temperature turbo-expander. The costs for catalytic reduction illustrate the generally expected trend of decreasing cost for pollution control as the plant capacity increases. Molecular sieve adsorption should be able to achieve emission standards which are very much lower than those which are currently required, even in the USA. The cost is, however, relatively high.

Emission standards for new sulphuric acid plants in Europe can be satisfactorily achieved by use of the double contact process. A reliable estimate for the extra production cost in plants in the 700-1000 tonne/d range is $0.42/tonne of sulphuric acid. The American estimates again illustrate the effect of increasing plant capacity on costs, but they are probably too low for reasons already discussed. An emission rate of 2 kg SO_2/tonne H_2SO_4 implies a conversion efficiency of 99.7%, which may be difficult to achieve consistently over a long period of operation. It may be necessary therefore to use one of the many tail-gas treatment methods to meet the American standards. The cost of pollution control would then be very much higher, and none of these methods can be said to be established for long-term full-scale operation.

It is difficult to make general estimates of the cost of scrubbing exhaust gases for fluorine removal. The cost of the scrubber depends upon the volume of gas that has to be treated and this will vary from plant to plant. The gas flows corresponding to the figures in Table 51 are given in the relevant sections of the report. The costs for the granulated triple superphosphate process are very high because of the complexity of the scrubbing system used. Multi-scrubber systems have also been proposed for use on compound fertilizer granulation plants, but here the costs are offset by the value of recovered materials. If abatement scrubbers are used to avoid the formation of a steam plume the cost is relatively high.

Water Pollution

Most of the processes for water pollution control which have been described in this report are still being developed. At the present time dilution of waste streams is frequently relied upon to reduce the concentration of contaminants in waste water to harmless levels and the only treatment which is applied is oil separation, possibly pH adjustment and the provision of settling ponds for the removal of suspended solids. This minimum level of treatment is sufficient to comply with water pollution regulations which are at present in force in Europe. There are signs, however, that stringent regulations on the discharge of nitrogen-containing waste water are likely to be more widely applied in the future. Some of the processes which might become generally available to meet higher effluent standards have been described and the costs of treatment by these processes were compared in Table 35.

Removal of nitrogen, phosphates and fluorides from fertilizer plant effluents is not yet widely practiced. On most sites these effluents will be mixed with waste streams from other processes. In this way it may be possible to adjust the pH to an acceptable value for discharge without addition of acid or alkali. It is, however, not possible to separate the portion of the cost of water pollution control which is applicable to the fertilizer processes. This situation will change if the standards which are being considered in the USA are taken up in Europe and the industry will need to adopt a great deal of new technology which is specific to the processes which it operates.

A detailed analysis of the economic impact of water pollution control costs on the fertilizer industry in the USA has been carried out in a recent report to the EPA[141]. Table 52 presents the estimated capital investment and annual operating and maintenance costs for effluent control techniques applicable to processes used in the manufacture of nitrogenous fertilizers. Although detailed technical descriptions of these control techniques were not given they are clearly similar to processes described in earlier sections of this report. Ion exchange and biological treatment are regarded as best available technology (to be achieved by July 1, 1983), while the remaining processes are regarded as best practicable technology (to be achieved by July 1, 1977). Details of proposed EPA regulations on the quality of the effluent to be achieved by these levels of effluent control are given in Appendix A.

All the quoted costs refer to 1972 price levels in the USA. In order to put the data in Table 52 on a basis comparable with other cost data in this report, investment-related costs have been re-calculated at the rate of 30% per annum. Significant extra man-power is only required for ion-exchange and biological treatment. Chromate removal, oil separation and biological treatment are applicable to all nitrogenous fertilizer processes.

Comparison of Tables 35 and 52 shows significant differences in cost estimates from different sources. This is particularly true for the urea hydrolysis/steam stripping process. The American estimates of both capital and running costs[141] are higher than the Dutch[90] though it is not clear whether the former include any credit for recovered ammonia. The estimated costs for steam stripping of ammonia plant condensate in Tables 2 and 52 are quite close, however, if it is assumed that the stripped ammonia is not vented to the atmosphere.

Table 52 shows the expected tendency of the control cost per tonne of product to decrease as the capacity of the plant increases. It also permits some interesting

TABLE 52. - Estimated Investment and Annual Running Costs for Effluent Control Technology in Nitrogenous Fertilizer Manufacture

Plant	Control Technique	Capacity, 1000 tonnes/y	Investment, $1000	Annual Costs: Investment Costs (at 30%), $1000	Annual Costs: Energy and Power, $1000	Annual Costs: Extra Man-power, $1000	Control Costs, $/tonne
Ammonia	Steam Stripping	45	91	27	83	-	2.44
		95	128	39	116		1.63
		190	181	54	164		1.15
		320	234	70	212		0.88
		480	299	90	269		0.75
Ammonium Nitrate	Ion Exchange	95	343	103	78	172	3.72
		145	430	129	98		2.75
		320	624	187	142		1.57
Urea	Hydrolysis/Steam Stripping (DSM Process)	47	97	29	63	-	1.96
		95	137	41	88		1.36
		145	171	51	111		1.12
		320	249	75	161		0.74
General Nitrogenous Fertilizers	Chromate Removal	190	58	17	13	-	0.16
	Oil Separation		17	5	5	-	0.05
	Biological Treatment		91	27	10	20	0.30
	Chromate Removal	320	76	23	21	-	0.14
	Oil Separation		22	7	6	-	0.04
	Biological Treatment		118	35	13	20	0.21
	Chromate Removal	480	97	29	31	-	0.13
	Oil Separation		28	8	8	-	0.03
	Biological Treatment		151	45	17	20	0.17

conclusions about the relative costs of the various control techniques. The costs for chromate removal and oil separation, techniques which are already used to some extent, are small compared with the newer processes for removal of nitrogen from the waste water. The costs for the two steam stripping processes are, not surprisingly of the same order of magnitude. Ion exchange is by far the most expensive of the control techniques to operate, in terms of both capital and running costs.

Table 53 presents cost data for effluent control in the manufacture of phosphate fertilizers. These data represent best practicable technology, with the exception of sulphuric acid dilution of pond water. The information is based upon the use of gypsum ponds and is therefore not directly relevant to most European plants. If fluorides are removed from waste water by treatment with lime before discharge to a river or estuary, the data in Table 53 probably give a realistic indication of the costs involved. No information is given in the American report[141] on the sulphuric acid dilution of pond water, or the effluent control techniques used in sulphuric acid and di-ammonium phosphate plants and it is therefore not possible to comment on the estimated costs here. Another report which contains this information has been produced[142] but a copy has not been made available.

The total cost of water pollution control for a product can be calculated by adding together the costs of the individual control techniques which are used. For example, in the case of ammonia production it will be necessary to use steam stripping, chromate removal, and oil separation in order to meet the regulations quoted in Appendix A. Products such as ammonium nitrate, urea, and phosphates require intermediate products for their manufacture. A proportion of the effluent control costs of the intermediate process will therefore contribute to the total control cost for the final product. Thus the total effluent control cost for ammonium nitrate will include costs for ion exchange and chromate removal, and also a pro-rata share of the costs applicable to the ammonia used in the production of the ammonium nitrate. Table 54 gives plant configurations and pro-rata factors for the estimation of cumulative effluent control costs for some fertilizer products. The information in Tables 52-54 can be combined to give estimates for various combinations of control techniques.

In a multi-plant complex common treatment facilities might be feasible. For example, a steam stripping facility might conceivably be used to treat the combined process condensates from several plants. Through economy of scale the net costs per tonne of product would be appreciably lower. If biological treatment facilities are installed, the greatest economy is obtained by combining waste waters containing organic materials with effluents from fertilizer processes.

An important aspect of pollution control costs is the effect they might have on premature plant closures. In order to make some quantitative predictions the capitalized value of future earnings was compared with the scrap value of plants of various sizes[141]. It was concluded that the capitalized value of plants of lower capacity than

TABLE 53. - Estimated Investment and Annual Running Costs for Effluent Control Technology in Phosphate Fertilizer Manufacture

Plant	Control Technique	Capacity, 1000 tonnes/y	Investment, $1000	Annual Investment Costs (at 30%), $1000	Annual Running Costs in $1000		Control Costs, $/tonne
					Materials	Energy and Power	
Phosphoric Acid	Pond water treatment (double liming)	75	376	113	161	6	3.73
		180					1.56
		310					0.90
	Pond water treatment (triple liming)	75	591	177	260	9	5.94
		180					2.48
		310					1.44
	Pond Seepage	75	176	53	-	5	0.77
		180					0.32
		310					0.19
	Pond Water - H_2SO_4 dilution	75	193	58	-	12	0.93
		180	299	90	-	18	0.60
		310	396	119	-	24	0.46
Sulphuric Acid	Effluent Control	230	211	63	-	4	0.29
		310	250	75	-	5	0.26
		540	345	104	-	7	0.21
		900	470	141	-	10	0.17
	Chromate Control	230	64	19	14	1	0.15
		310	76	23	19	1	0.14
		540	105	32	33	1	0.12
		900	143	43	55	2	0.11
Di-ammonium Phosphate	Effluent Control	150	235	71	-	259	2.20
		300	337	101	-	371	1.57
		650	520	156	-	572	1.12

TABLE 54. - Plant Sizes, Configurations and Pro-rata Factors for Estimation of Cumulative Effluent Control Costs

Product		Intermediate Products					
		Ammonia		Sulphuric Acid		Phosphoric Acid	
Process	Capacity, 1000 tonnes/y	Capacity Required, 1000 tonnes/y	Pro-rata factor, %	Capacity Required, 1000 tonnes/y	Pro-rata factor, %	Capacity Required, 1000 tonnes/y	Pro-rata factor, %
Ammonium Nitrate	95	190	11				
	145	190	17				
	320	320	22				
Urea	47	95	30				
	95	190	30				
	145	320	28				
	320	480	41				
Di-ammonium Phosphate	150	45	78	230	100	75	100
	300	95	72	540	78	180	78
	650	190	79	900	100	310	100
Triple Superphosphate	150			230	71	75	71

those listed below would be less than their scrap value. Such plants would be likely candidates for closure, but they are likely to be old plants of obsolescent design:

Ammonia	105 000 tonnes/y
Ammonium Nitrate	105 000 "
Urea	52 000 "
Di-ammonium Phosphate	100 000 "

General Conclusions

A general comment about all the pollution control costs quoted in this report is that they have been calculated assuming 100% utilization of capacity. This is unlikely to be achieved in the early years of the life of a plant and the cost of pollution control will therefore be initially considerably higher than the estimates which have been made. A further point which must be considered is the crude method which has been used to estimate control costs. A fertilizer manufacturer will be interested in the increase in price which will be necessary to maintain the same rate of return on investment after pollution control technology has been installed. Because of the discounting procedure used in estimating rates of return, this price increase will be higher than the simple cost of control per tonne of product. It is felt, however, that it would only be possible to make more sophisticated calculations of the effect of pollution control on the rate of return on investment for a specific plant on the basis of accurate cost data applicable to the site.

The most important effluents from the fertilizer processes under consideration are summarized in Table 55. As far as possible estimates have been made of the quantities of each effluent which might be discharged from a typical plant. It must be emphasized once again that the figures quoted are based upon the limited amount of information which is available, and that quite wide variations may occur from plant to plant. The estimated figures are considered to be most accurate for ammonia, nitric acid, sulphuric acid and phosphoric acid plants, because of the relatively large amount of available information about these processes. The Table also quotes estimates of the reduced effluent levels which are possible using the best modern technology.

Several of the processes produce water as a condensate which must be removed. This happens in the production of ammonia, ammonium nitrate and urea. The condensates tend to be contaminated and at the present time they probably make a major contribution to the aqueous effluent from most plants. As discussed in the relevant sections of this report, processes are available to remove and recycle the contaminants and produce water which is suitable for re-use in the plant. These processes have not yet achieved widespread application and may require further development work.

The figures for the typical effluent from a nitric acid plant correspond to nitrogen dioxide concentrations of 1000-3000 ppm. The higher level would not impose any

TABLE 55. - Summary of the Most Important Effluents from Fertilizer Processes

Product	Source of Pollution	Pollutant	Destination	Effluent Discharged in kg/ Tonne of Product	
				Typical Effluent*	Best Technology
Ammonia	process condensate	NH_3	water	0.6-1.2	0.03
		CO_2		1.0-3.1	0.06
		Methanol		0.8-4.8	0.08
Nitric Acid	tail gas	NO_x (as NO_2)	air	7-20	1.5-4.5
Sulphuric Acid (Contact Process)	tail gas	SO_2	air	13	2-3
		acid mist		0.3-7.0	0.04-0.08
	scrubber acid (metallurgical plants)	dilute H_2SO_4 (15-30%)	water	10-50	-
Phosphoric Acid (Dihydrate Process)	reactor and concentrator	F	air	0.002-0.15	<0.02
	scrubbing	F	water	40	4 (with F recovery)
	concentrator	P_2O_5	water	2	-
	filter cake	gypsum	water or dry dumping	5000	-
Superphosphate	mixer and den	F	air	0.04 - 0.2	-
	including storage pile	F	air	possibly >1.0	-
Ammonium Nitrate	neutralizer vapour	NH_3, NO_3	air	6-12 as AN	<2.5 as NH_3, no NO_3
	condensate	NH_3, NO_3	water	6-12	<2.5
	prilling tower	NH_3 and fume	air	-	<0.5
	prilling tower	dust		2	<1
MAP	spray drier	dust	air	0.75	-
Granular NPK Fertilizer (TVA-type process)	pre-neutralizer and granulator	NH_3	air	-	1.4
		dust		-	0.2-0.4
		F		-	0.004-0.04
	F scrubber	F	water	0.4 - 4	-
Urea	reaction loop	NH_3	air	0.32	-
	concentrator	NH_3	water	0.16	0.03
	concentrator	urea		1.6	0.11
	prilling tower	NH_3	air	0.48	-
		urea		1.33	-

*Typical effluent here refers to an average composition based upon information in this report. It is quite possible that the effluents from some plants will have compositions outside the quoted ranges.

severe penalty on the operation of a new plant. Any modern nitric acid plant could be expected to achieve this level on economic grounds alone. Recent practice in the United Kingdom has been to design for a limit of 1000-1500 ppm by increased absorption capacity, with the possibility of using catalytic reduction for decolourization and power recovery. The Alkali Inspectorate is now asking for 1000 ppm and a colourless plume. An American estimate has shown that capital and fuel costs for decolourization are offset by power recovery and the net cost per tonne of nitric acid is very low, but the truth of this statement will depend upon the cost of fuel prevailing at the site. In Europe, where low-temperature tail-gas expanders are used, the economics would depend upon the credit applicable to power recovery in the form of steam, and this may vary considerably from site to site.

The proposed American emission standard of 320 ppm for existing plants will not be achieved easily with present technology. Modifications to existing plants are likely to be extremely expensive and manufacturers may prefer to invest in new equipment. The emission standard of 200 ppm for new plants is probably within the reach of the best modern technology. There are several possible techniques available. With the provision of extra absorption capacity is is claimed that it is possible to reduce the concentration of nitrogen oxides to 200-600 ppm, depending upon the process and the absorption pressure. This method would be particularly favourable in a mixed pressure process where it is possible to use absorption pressures as high as 12-13 atmospheres. Caustic scrubbing is still being used in some new plants to reduce nitrogen oxide concentrations to similar levels. Finally, there are signs that catalytic reduction may become more acceptable in the near future, its long-term reliability and effectiveness having been demonstrated recently. The estimates in this report do not show a clear preference in terms of cost between extended absorption capacity and catalytic reduction, although the running cost of the latter technique is likely to increase rapidly with increasing fuel costs.

Each of these control techniques has its disadvantages. Catalytic reduction is wasteful, in that it destroys valuable raw materials. In addition there will still be some air pollution from unburned fuel, carbon monoxide, ammonia and possibly hydrogen cyanide in the tail-gas. Also, it is not possible to run the reduction unit during start-up and shut-down of the nitric acid plant and very much higher emission levels will result at these times. This limitation does not apply to the use of increased absorption capacity. On the other hand, it has been claimed that the absorption system may be more sensitive to running above design capacity than a catalytic reducer[21]. Caustic scrubbing is effective, but introduces a by-product with an associated disposal problem. The best answer, if it becomes commercially established, may be molecular sieve adsorption. It should be possible to operate this system continuously and it should prove to be flexible. It may also be relatively easy to fit this system to existing plants. Present estimates indicate that it is the most expensive of the control techniques.

Trends in nitric acid technology would be greatly affected by the development of a successful non-noble metal catalyst. The incentive for low-pressure ammonia conversion would be considerably reduced. This could produce a trend to higher mono-pressure nitric acid plants, thus ameliorating the pollution problem more economically.

Technology for reducing the sulphur dioxide emissions from a sulphuric acid plant to less than 500 ppm is now well established. Dispersion of the tail-gas from a sulphuric acid plant is not very good because of its low temperature (approx. 60°C). It seems unlikely that concentrations higher than 500 ppm will be considered to be acceptable from new sulphuric acid plants, which are therefore likely to be double contact plants. The additional cost involved appears to be reasonable at the present time. Lower concentrations of sulphur dioxide can be achieved by wet scrubbing, but the available processes have a number of disadvantages. These include high cost, the production of a by-product which may raise disposal problems, and reduction of buoyancy of the waste gases. The new fibre mist eliminators are very effective, so that dense white plumes of acid mist can no longer be regarded as acceptable. As in the case of nitric acid, adaption of existing plants to meet American emission standards would be difficult and expensive.

Control of fluoride emission to the atmosphere is relatively inexpensive and the installation of a simple scrubber on the reactor of phosphoric acid and superphosphate plants is standard practice. There is a wide variation in the quantity of fluorine discharged from different plants, but modern designs of wet scrubber should be able to achieve less than 0.02 kg of fluorine/tonne of product at reasonable cost. Discharge of scrubber liquors and barometric condenser water to water courses can be the cause of considerable pollution by fluorides but the amount of water discharged can be greatly reduced by recirculation. This procedure is probably more likely to be carried out at inland sites than at coastal sites. Fluorine recovery at the present time is practised only on a limited scale because of the small market for fluorosilicic acid. The increasing demand for fluorides, combined with more stringent water pollution legislation, may act as a spur for the further development and application of commercial processes for the manufacture of such materials as aluminium fluoride, calcium fluoride and hydrofluoric acid. It appears that these products could become competitive with products made from fluorspar, the only high-grade fluoride ore now available.

Disposal of by-product gypsum is a big problem particularly from phosphoric acid plants which are not near the coast. Lack of space for dumping of dry dypsum on land has led to an increasing interest in possible uses for the gypsum, particularly in Germany. Economically the returns must be very small because of the availability of natural gypsum at a low price. Expansion of this field therefore appears to be considerably less likely than expansion in the recovery of fluorides.

There is a wide variation in the processes and formulations used in the manufacture of compound and complex fertilizers. Only a very limited quantity of data is available on the effluents from these processes, and much of this information refers to plants outside the EEC. It is possible, however, to come to a few conclusions which may be generally valid.

Losses of ammonia and fertilizer dust can be quite high in both nitrophosphate- and ammonium phosphate-based processes. It is economically attractive to recover as much as possible of these materials and return them to the processes. To avoid merely substituting a water pollution problem for an air pollution problem it is necessary to recirculate the scrubber liquors to the process. The capital investment involved will be greater than for simple once-through scrubbing systems, but recovery of raw materials can recover at least part of the cost. The use of complex multi-scrubber systems will, however, make operation of the plant much more difficult.

Control of fluoride emissions to the atmosphere is easily carried out, but here it is likely that a water pollution problem will be created that can only be partially ameliorated by recycling. No instances are known of fluorine emissions from these processes being recovered for sale. The total fluoride discharged to the environment is minimized in nitrophosphate processes.

The use of nitrophosphate processes also reduces the total quantity of gypsum discharged to the environment in compound fertilizer manufacture. If the calcium is removed as carbonate or sulphate and dumped on dry land, however, the potential pollution hazard may be greater than that which would occur from gypsum from phosphoric acid manufacture. This is because the nitrophosphate waste would contain nitrogen as well as phosphorus, and nitrogen is more likely to be leached into the soil and surface waters.

Because of the wide variation in compound fertilizer processes, the figures quoted in Table 55 for losses to the atmosphere are those available for the degree of control that is available with the best proven technology. With such a system the losses to the atmosphere should be of the same order of magnitude for both nitrophosphate and ammonium phosphate-based processes.

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LEGISLATION ON POLLUTION RELATING TO THE FERTILIZER INDUSTRY

EEC Countries

The ISMA/APEA Working Party on Pollution in the Fertilizer Industry has carried out an enquiry into legislation relating to the fertilizer industry in several European countries. The author is grateful to ISMA for supplying a copy of a draft report and for permission to make use of the information in this report. Tables A1 and A2 summarizing air and water pollution regulations in EEC countries, are based upon the ISMA/APEA enquiry, supplemented with information obtained from other sources.

USA

Information about proposed and existing legislation in the USA has been kindly supplied by The Fertilizer Institute of Washington D.C. The Federal EPA has published firm regulations on new sulphuric and nitric acid plants in terms of SO_2 and NO_x. Individual states have jurisdiction over existing plants but EPA has suggested limits which most states are adopting. These emission standards, expressed in kg/tonne of 100% acid, are:

	New Plant	Existing Plants
SO_2	2.0	3.25
NO_x	1.5	2.25

Proposed figures for limitations on the emissions of fluorides are given below:

	kg/F/tonne P_2O_5
Wet Process Phosphoric Acid	0.01
DAP	0.03
Run-of-pile Triple Superphosphate (and storage)	0.10
Granular Triple Superphosphate	0.10
Granular Triple Superphosphate Storage (per hour in storage)	0.00025

TABLE A1. - Air Pollution Regulations in EEC Countries

Country	Maximum Local Emission Values		Statutory Ground Level Concentration Limits (Immission Values)	
Belgium	A few factories have statutory limits:		SO_2	0.5 mg/m^3 - 30 min average
	NO_x	5000 mg/m^3		0.28 mg/m^3- 24h average
	SO_2	5000 mg/m^3		0.15 mg/m^3- annual average
	Dust	670 mg/m^3	Dust	0.85 g/m^2 d^{-1} - annual average
			Deposition	1.30 g/m d^{-1} - monthly average
Denmark	New regulations in preparation		In preparation	
France	No statutory limits		SO_2	0.25 mg/m^3 - 24h average
			Dust	0.15 mg/m^3 - 24h average
Germany	Regulations published in VDI guides (Verein Deutscher Ingenieure)		NO_x (as NO_2)	1.0 mg/m^3 - 30 min average
	HNO_3 plants - guide 2295 (August 1968):			2.0 mg/m^3 - one 30 min period in 8h
	Low pressure plants	4.0 g NO/m^3	SO_2	0.4 mg/m^3 - 30 min average
	Medium pressure plants	1.5-3.0 g NO/m^3		0.75 mg/m^3 - one 30 min period in 2 h
	High pressure plants	1.0-2.5 g NO/m^3	Dust (industrial areas)	
	These regulations are under revision. It is anticipated that NO_x emissions for all kinds of plants will be limited to 1 g NO/m^3 or lower.			0.85 g/m^2 d^{-1} annual average
	Alkali absorption of NO_x only permitted if nitrite solution used on site. Catalytic reduction is regarded as beyond existing technology.			1.30 g/m^2 d^{-1} monthly average
	H_2SO_4 plants - guide 2298 (June 1968):			
	Double contact plant	minimum SO_2 conversion 99%, acid mist 0.4 kgSO_3/tonne H_2SO_4		
	Contact Plant without intermediate absorption	Only to be used when SO_2 content in feed gas <6%, minimum SO_2 conversion 97.5%, acid mist 0.6 kg SO_3/tonne H_2SO_4		
	Metallurgical Plants	minimum SO_2 conversion 97.5%, acid mist 2 kg SO_3/tonne H_2SO_4		
	Chamber plants	SO_2 5 mg/m^3 NO_2 1.2 g/m^3		
	Fluorides:			
	Limits for several factories e.g. 20 mg/m^3 as HF.			
	A restriction is under consideration for HF emissions from superphosphate plants - for HF emission of 150 g/h the concentration of HF in the exhaust gas should not exceed 5 mgF/m^3			
	Dust:	50-150 mg/m^3		

TABLE A1 (contd)

Country	Maximum Local Emission Values	Statutory Ground Level Concentration Limits (Immission Values)
Italy	No statutory limits but emission values must be compatible with ground level concentration values	30 min average / 24 h average NO_x 0.79 mg/m^3 / 0.39 mg/m^3 SO_2 0.56 " / 0.19 " HF 0.06 " / 0.02 " HCl 0.30 " / 0.05 " Dust 0.75 " / 0.30 "
Netherlands	Some factories have statutory limits e.g. factory a: SO_2 3100 kg/d SO_3 250 mg/m^3 factory b: SO_2 600 kg/d (treatment of tail gases required) SO_3 250 mg/m^3 factory c: HF 10-175 kg/d factory d: NO_x 3000 ppm (by volume) $\sim$6.0g NO_2/m^3	At the end of 1972 no legal limits known. Dutch Council of Health has proposed for SO_2 and smoke combined: % of measurements less than stated concentration / SO_2 mg/m^3 $24h^{-1}$ / Smoke mg/m^3 $24h^{-1}$ 50 / 0.075 / 0.03 98 / 0.25 / 0.09 Other compounds: in general the German limits
United Kingdom	Alkali Inspectorate's Presumptive Limits: HNO_3 plants: total acidity 4.6 g/m^3 as SO_3 ($\sim$2700 ppm NO_2). Recently built plants have guaranteed 1000-1500 ppm NO_2; 1000 ppm NO_2 and decolourization likely to be asked for in future. H_2SO_4 plants: SO_2 max 2% of S burned in older plants max 0.5% of S burned in new plants Plants other than S burning plants - acidity 9.2 g/m^3 as SO_3; gases discharged from all plants must be free from acid droplets and persistent mist Phosphoric Acid and Superphosphate plants: total acidity 0.23 g/m^3 as SO_3 (324 mg/m^3F) *or* efficiency of condensation of acid gases >99% Granulation plants: HCl 0.46 g/m^3 as SO_3 Dust 0.46 g/m^3 NH_3 acid scrubber required to minimize emissions	The height of the chimney should be such that the calculated 3 minute mean ground level concentration for a wind speed of 32 km/h does not exceed: 0.14 - 0.20 ppm SO_2 for H_2SO_4 plants 0.14 - 0.16 ppm NO_2 for HNO_3 plants In general maximum ground level concentrations are taken as one thirtieth of the maximum concentration recommended for eight hour occupational exposure in factories.

<u>TABLE A2. - Water Pollution Regulations in EEC Countries</u>

Country	Regulations
Belgium	Discharge standards vary according to the receiving river. One factory is forbidden to discharge gypsum into the river, another is permitted to discharge gypsum into a tidal river on the ebb tide only.
Denmark	Regulations in preparation
France	pH 5.5-8.5 Suspended Solids 30 g/m^3 BOD 40 g/m^3 No poisonous substances
Germany	1957 Wasserhaushaltsgesetz with amendments up to 1970 requires permits for use of surface, ground or immediate coastal waters. No discharges to underground waters. The Government intends to introduce levies and use the revenue to build treatment plants. The "polluter pays" principle is not legally the case at present, but it occurs to a limited extent in practice e.g. one chemical manufacturer with 17,000 employees discharges 7,200 m^3/day and pays DM 0.8-1.0 million per annum.
Italy	Permission for discharge required from Public Health Office
Netherlands	1969 Surface water pollution act came into force at the end of 1970. It introduced a system of levies which vary from one water authority to another. In 1972, DFl 7.5-9.5 per population equivalent* for industrial discharges Levies will rise by 10% p.a. to DFl 20 over the whole country by 1977
United Kingdom	For plants built after 1960, inland or estuary discharges under control of water authorities. After 1975 discharges from older plants will also be controlled. River authorities often base limits on "Royal Commission 30:20 Standard" i.e. 30 g/m^3 suspended solids, 20 g/m^3 BOD. 20:15, 15:10, 10:10 and even more stringent standards are applied in practice when warranted by local conditions. Some river authorities lay down ammonia limits, usually when there is little dilution and water is abstracted for potable supply down stream. Usual standard: 10 g/m^3 ammoniacal N. Other typical standards applicable to fertilizer industry: pH 6-9 Temp $20^\circ C$ Free chlorine 1.0 g/m^3 Oil and grease 5.0 g/m^3 Total toxic metals 0.5 g/m^3

*Population equivalent is defined in Appendix B.

TABLE A3. - Proposed EPA Schedule A Limits on Effluents from Fertilizer Processes

	Units per tonne of product	Sulphuric Acid	Phosphoric Acid	Phosphate Fertilizers	Ammonia*	Ammonium Sulphate	Urea	Nitric Acid	Ammonium Nitrate
Total Flow	m^3	0.5	12.5	4.1	2.6	1.0	1.6	1.4	1.25
Fe	g	0.5	12.5	4.1	2.6	1.5	1.6	1.4	1.25
Suspended Solids	"	12.5	312.5	102.5	65	25	40	36	31.25
V	"	0.5	-	-	-	-	-	-	-
Se	"	0.25	-	-	-	-	-	-	-
As	"	0.125	-	-	-	-	-	-	-
F	"	-	62.5	20.5	-	-	-	-	-
NH_3-N	"	-	-	-	-	10	16-48†	14	12.5
Heavy Metals	"	-	12.5	4.1	-	-	-	-	-
Cd	"	-	2.5	0.8	-	-	-	-	-
Ni	"	-	-	-	1.3	0.5	0.8	0.7	0.625
Kjeldahl-N	"	-	-	-	26	-	-	-	-
Oil	"	-	-	-	26	-	16	14	12.5
Organic-N	"	-	-	-	-	-	16-48†	-	-
Co	"	-	-	-	-	-	0.8	0.7	-
NO_3-N	"	-	-	-	-	-	-	14	12.5

*Plants with Centrifugal Compressors

†Lower limit for once-through processes, higher limit for total recycle processes

Water pollution regulations are still in the formative stages and there is still some controversy between EPA and the industry on whether present technology is capable of achieving the effluent levels which have been published. A summary of "Schedule A" values[141] which were published in October 1972 is given in Table A3, and the concentrations of contaminants in the effluent to which these figures correspond are given in Table A4. A detailed technical rationale for these figures has been given in an unpublished report[143], but it has not been possible to obtain a copy of this report.

TABLE A4. - Proposed EPA Regulations for Fertilizer Plant Effluents

Contaminant	Concentration g/m^3	Contaminant	Concentration g/m^3
Fe	1.0	Cd	0.2
Suspended Solids	25	N_1	0.5
V	1.0	Kjeldahl-N	10
Se	0.5	Oil	10
As	0.25	Organic-N	10
F	5.0	Co	0.5
NH_3-N	10	NO_3-N	10
Heavy Metals	1.0		

The figures below have been recently proposed for sulphuric acid plants and phosphate and nitrogen fertilizer complexes in terms of Levels I, II and III. Level I is the effluent level that plants must meet by July 1, 1977 and represents "best practicable control technology". Level II is the target for July 1983, representing "best available control technology". Level III is for new sources, started after official publication of the limitations. The pH must in all cases be ± 1.0 pH unit from the pH of the receiving stream and within the range 6.0-9.0.

Sulphuric Acid Plant

Level in g/tonne 100% H_2SO_4

	I	II	III
Cr	2.65	2.65	2.65
Zn	5.3	5.3	5.3
SO_4	410	205	205

These limits presumably refer to the cooling water effluent stream.

Phosphate Fertilizer Complex

Level in g/m^3

	I	II	III	Schedule A
N	25	No discharge*		-
P	40	"		10
F	15	"		10
Suspended Solids	25	"		50

*except under
abnormal "Act of God"
circumstances

Nitrogen Complex (Ammonia, Ammonium Nitrate, Nitric Acid, Urea)

Level in g/tonne of product

	I	II	III	Schedule A
NH_3-N	87.5*	37.5	37.5	68.5-102.5
NO_3-N	75	50	75	26.5
Organic-N	125	50	75	16-50
	287.5	137.5	187.5	111-179
Cr	2.65	2.65	2.65	-
Zn	5.3	5.3	5.3	-
Oil, grease	26.5	26.5	26.5	68.5

* 52.5g for a single ammonia plant

DEFINITIONS AND CONVERSION FACTORS

Population Equivalent

One population equivalent denotes the average amount of waste material discharged daily with effluent water for each inhabitant of a country. This per capita amount of waste material is quantified as:

1. Chemical Oxygen Demand or COD = 135 g/d
2. Ammonia nitrogen to be disposed of = 10 g/d

Approximately 45g of oxygen is required to oxidize 10 g of ammonia. The population equivalent is given by the formula

$$\text{P.E.} = \frac{\text{COD in g/d} + 4.57 \times \text{ammonia N in g/d}}{135 + 45}$$

For a urea plant condensate

$$\text{P.E.} = \frac{4.57 \times \text{ammonia in g/d}}{180}$$

Concentrations of Gaseous Pollutants:

Concentrations of gaseous pollutants are usually quoted either in parts per million by volume, or in mg/m^3. The latter term is now preferred. Some useful factors for conversion of 1 ppm at 20°C into mg/m^3 are:

NH_3	0.7
F	0.8
NO_2	1.91
SO_2	2.66
H_2SO_4	4.08

Concentrations of Aqueous Pollutants

It is becoming standard practice to quote concentrations in g/m^3 rather than mg/l, but the numerical value is unchanged by this change of units.

PRODUCTION OF FERTILIZERS BY COUNTRY IN 1971[124]

Country	Synthetic Ammonia 1000 tonnes N	Nitrogenous Fertilizers from Synthetic Ammonia 1000 tonnes N	Urea	Phosphoric Acid in 1000 tonnes P_2O_5		Phosphate Fertilizers in 1000 tonnes P_2O_5			
				Thermal	Wet Process	SSP	TSP	Other Simple Phosphates	Complex Fertilizers
Belgium	545	405	72	-	376	27	216	nd	308
Denmark	nd	nd	nd	-	nd	69	-	nd	26
France	1758	1647	148	38	639	289	247	74	601
Germany	1788	1227	nd	nd	nd	46	-	132	433
Ireland	nd	nd	nd	-	nd	nd	nd	nd	nd
Italy	1270	671	nd	-	nd	193	22	1	294
Netherlands	1550	561	309	-	329	32	65	-	176
UK	nd	nd	nd	-	nd	51	42	14	324

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Fig. 1	L-5548-AP
Fig. 2	L-5549-AP
Fig. 3	L-5550-AP
Fig. 4	L-5551-AP
Fig. 5	L-5552-AP
Fig. 6	L-5553-AP
Fig. 7	L-5554-AP
Fig. 8	L-5556-AP
Fig. 9	L-5557-AP
Fig.10	L-5558-AP
Fig.11	L-5559-AP
Fig.12	L-5560-AP
Fig.13	L-5561-AP