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MODERN TECHNOLOGY FOR MINIMIZING POLLUTION FROM FERTILIZER PLANTS[1]

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CONTENTS

INTRODUCTION

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. This paper reviews the pollution control techniques which can be applied to the various processes used in the manufacture of fertilizers.

I. AMMONIA

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. The only control technique used for the continuous emissions is dispersion from a high stack, and intermittent escapes of ammonia can be minimized by careful plant maintenance. The major pollution problem from an ammonia plant is the aqueous process condensate.

When the process gas stream from the reformer is cooled the process condensate is formed from the unreacted steam. The condensate 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 material.

The actual composition of the process condensate in any plant will depend upon the reformer catalyst used, but two examples are given in Table 1.

TABLE 1. Composition of Ammonia Plant Process Condensate

Quantity, m^3/tonne NH_3	Concentration of Components, g/m^3			Reference
	Ammonia	Carbon Dioxide	Methanol	
1.2	1000	2600	2000-4000	1
1.5	400	700	500	2

In addition, small concentrations (ie a few g/m^3) of methylamine have been detected in the condensate from some plants.

Ammonia can be stripped from the condensate by raising the pH of the waste water to 10.5 - 11.5 and providing sufficient air-water contact. 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. 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.

A process has been developed which uses steam to remove most of the ammonia and organic material from the condensate and allows the stripped condensate to be used as boiler feed water[1,3]. 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 g/m^3 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. 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.

II. NITRIC ACID

The only continuous source of pollution from a nitric acid plant is the tail-gas from the absorption tower which contains oxides of nitrogen. The composition of the tail-gas depends upon the efficiency of the absorption system. All modern processes carry out absorption at not less than 3 atmospheres, achieving absorption efficiencies of between 98.2 and 99.3%[4]. 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.

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[5-7]. The techniques used fall into five classes:

Wet Scrubbing
Dilution and Dispersion
Increased Absorption Capacity
Catalytic Reduction
Adsorption

A. 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[8] and concentrations as low as 100 ppm have been achieved[9]. 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[7] but none of these has achieved commercial application.

B. Dilution and Dispersion

The policy of dilution of the tail-gas by mixing with additional air or steam is widely employed, 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. Even when other control measures are used it is still a wise precaution to provide a high stack as a safety measure for occasions when the plant is not operated at optimum efficiency.

C. 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. It is, of course, an advantage to have a high absorption pressure and 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 absorption, but 600 ppm is probably a reasonable average for high pressure plants with extended absorption capacity.

D. 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. It was found that the nitrogen dioxide reacted simultaneously with the fuel to yield nitric oxide, thus causing decolourization of the effluent gas.

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:

$$CH_4 + 4NO_2 \longrightarrow 4NO + CO_2 + 2H_2O \text{ ....} (1)$$

$$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2H_2O \text{ ....} (2)$$

$$CH_4 + 4NO \longrightarrow 2N_2 + CO_2 + 2H_2O \text{ ....} (3)$$

Similar equations can be written substituting hydrogen for methane. The decolourization reaction (1) is faster than reaction (2), and decolourization can therefore be achieved in the presence of oxygen. The abatement reaction (3), on the other hand, is much slower than reaction (2). In order to reduce the nitrogen oxides to nitrogen sufficient fuel must be added to react with all the oxygen in the tail-gas. 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.

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. 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[10]. A plant in Belgium 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.

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[11]. 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[12]. 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:

$$8NH_3 + 6NO_2 \longrightarrow 7N_2 + 12H_2O \quad \ldots\ldots\ldots\ldots \quad (4)$$

$$4NH_3 + 6NO \longrightarrow 5N_2 + 6H_2O \quad \ldots\ldots\ldots\ldots \quad (5)$$

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.

E. 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. A Molecular Sieve Process has been developed in the United States[13,14]. 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.

III. SULPHURIC ACID

Consideration will be restricted here to sulphur-burning contact plants, where the only continuous source of pollution is the tail-gas. A conventional contact plant can be designed to operate at a maximum sulphur dioxide conversion efficiency of around 98.5%. The residual sulphur dioxide concentration in the tail-gas should be in the range 1800-2000 ppm. In addition to sulphur dioxide, sulphuric acid mist is often emitted, and thus gives rise to a dense white plume. The mechanism of formation of the acid mist is not well understood, and plant contractors are generally unwilling to give guarantees for acid mist emissions unless mist eliminators are fitted.

By far the most important and widely used method reducing sulphur dioxide emissions at the present time is the "double contact" process.

Various methods of tail-gas treatment have been suggested, but none has achieved widespread commercial exploitation. Operation at high pressure favours sulphur dioxide conversion, and a pressure plant has been built in France for which an efficiency of 99.85% has been claimed[15,16].

A. 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[17]. 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[17].

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, and the technology is well established. The process requires an additional heat exchanger and absorption tower which add to the capital cost of the plant. To some extent this 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.

B. 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 were 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.

Most of the processes which have found commercial application are based upon ammonia scrubbing. 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[18]. Ammonium sulphate is today a relatively undesirable by-product and problems of disposal or sale have therefore limited the application of this type of process. A process in operation in Rumania[19] 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 Czechoslovakia uses nitric acid for sulphur dioxide regeneration and yields a dilute solution of ammonium nitrate.

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 molecular sieve system for sulphur dioxide recovery has been installed on a 180 tonne/d sulphuric acid plant in the USA[14]. 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.

IV. PHOSPHORIC ACID AND SUPERPHOSPHATES

The main problems are the evolution of fluorides during digestion of phosphate rock and phosphoric acid concentration, and the disposal of by-product gypsum during wet process phosphoric acid manufacture. Detailed consideration of these topics has been given in Slack's monograph on phosphoric acid[20].

A. Control of Gaseous Fluoride Emissions

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:

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

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, in order 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.

Because of the problems caused by the precipitation of silica the simpler types of scrubber are usually preferred. 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. Cyclonic spray scrubbers have also been popular. Impingement and Venturi scrubbers are capable of higher efficiencies, but running costs are relatively high because of the high pressure drop required. In wet process plants in which the reaction chamber is cooled by vacuum cooling, and vacuum concentration plants the fluorine is absorbed in the barometric condenser water, so that air pollution control is built into the system.

B. Fluorine Recovery

Air pollution control in phosphoric acid and superphosphate plants gives rise to an aqueous effluent containing substantial quantities of fluorine. This has given rise to attempts to recover fluorides as a by-product.

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. The economics of fluorine recovery from reactor vapours are much less favourable. It is only possible to recover approximately 2 kg of fluorine/tonne of P_2O_5 from air-cooled reactors, and this is reduced to about 1 kg/tonne of P_2O_5 from vacuum-cooled reactors.

Two commercial processes have been patented for use with a vacuum evaporation system[21]. In the simpler and more popular of these two processes 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.

The market for fluorosilicic acid is quite small, but there is an increasing demand for fluorides in industry, and with this in mind a number of processes have been developed for the manufacture of saleable products from fluorosilicic acid[22].

The only process to have reached commercial scale in Europe was developed in Austria. 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[23]. 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. By-product fluorosilicic acid from the production of 1600 tonnes/d of phosphoric acid could produce 100 tonnes/d of AlF_3.

C. Disposal and Use of By-Product Gypsum

In the manufacture of phosphoric acid around 5 tonnes of gypsum are produced per tonne of P_2O_5 and this constitutes a major disposal problem. Wherever possible the gypsum is disposed of by pipeline into seawater. In most countries disposal into inland rivers is not allowed. Other, less satisfactory disposal methods include the use of gypsum settling ponds and dumping on land, or in mines or excavated areas. As alternatives to disposal a number of processes which can use by-product gypsum have been proposed.

a) 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.

b) 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_2O_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, but a plant has been built in South Africa which uses exclusively by-product gypsum[24].

c) Lime-Sulphuric Acid

A process which uses carbon monoxide to reduce calcium sulphate to sulphur dioxide and lime has been developed[25]. It is claimed that the process is more economical to operate than the cement-sulphuric acid process, but it has not achieved commercial exploitation.

d) Plaster and Plasterboard

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. A process for the manufacture of plasterboard was developed in the UK but production has now ceased[26]. 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, however, another process is gaining acceptance[27]. 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 started production in 1973.

V. AMMONIUM NITRATE

The dangers of combustion and explosion when ammonium nitrate is handled give 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. The principles of the design of an ammonium nitrate plant taking into account the dual requirements of safety and effluent control have been described[28].

Nitrogen losses in the neutralizer can be minimized by lowering the pH, but this increases the hazards involved in handling the concentrated liquor. The problem can be solved by 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 and nitrogen efficiencies greater than 99% are possible. Careful pH control is necessary to achieve satisfactory operation of such a system[28].

If the steam from the neutralizer is condensed this gives rise to an aqueous effluent problem. Approximately 0.5 tonnes of water will be produced per tonne of ammonium nitrate, and the 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[29]. 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.

The other major source of pollution in an ammonium nitrate plant is the prilling tower. The effluent can contain ammonium nitrate dust, ammonium nitrate fume, and free ammonia. The dust arises because of the carry-over of micro-prills in the air stream, while the evolution of ammonia and fume depends upon melt pH, melt temperature and the air velocity over the surface of the melt[28].

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. Nevertheless it is possible to design an ammonium nitrate plant to give very low effluent levels and nitrogen losses from the prilling tower can be kept to less than 0.1%. Pollution control to these standards, however, requires high capital investment amounting to 25% of the capital cost of the plant.

VI. UREA

There will be losses of ammonia and urea dust from the prilling tower, and similar considerations to those discussed above apply. Concentrations of 40 mg/m^3 of ammonia and 110 mg/m^3 of dust have been quoted for one modern process[30]. Dust loadings as high as 500-1000 mg/m^3 are quoted for a Japanese process[31] but here the air is ducted down to a simple scrubber in order to reduce the dust concentration to 80-100 mg/m^3.

The condensate from the concentrator 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. A two stage process has been developed in which urea is hydrolyzed to ammonia at 180°C and the ammonia is recovered by stripping with steam[30]. In this process the urea concentration is reduced from 3000 g/m^3 to 200 g/m^3, and the ammonia concentration is reduced from 600 g/m^3 to 100 g/m^3.

VII. TREATMENT OF WASTE WATERS FROM NITROGENOUS FERTILIZER PLANT

A. Ion Exchange

An ion exchange plant for the removal of high concentrations of ammoniacal nitrogen and nitrate nitrogen has been built in the USA[32,33]. The plant consists of a moving-bed, continuous flow, countercurrent ion exchange system. There are two separate ion exchange systems, 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[33] 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 mg/l. The concentration of recovered ammonium nitrate, however, has been running at under 15%, which is much too low for the production of solid fertilizers and has even created problems in recycling it into liquid fertilizer products. Ion exchange therefore requires further development as a recovery technique.

B. Biological Treatment

Major schemes have been announced for the biological treatment of effluents (including those from fertilizer processes) in the Netherlands and Germany[34]. The Dutch scheme[35,36] is a four-stage process which is a development of an existing process for the treatment of bio-degradable organic substances. The first step uses the organic materials present in the effluent as a source of COD for the biological reduction of nitrate under anaerobic conditions. 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. The effect of the present and proposed future purification plants on the composition of the overall effluent is summarized in Table 2.

TABLE 2. 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 COD reduction	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

VIII. GRANULAR COMPOUND AND COMPLEX FERTILIZERS

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 (from nitrophosphate processes), 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.

It is standard practice to use a combination of dry cyclones and wet scrubbers to reduce emissions to the atmosphere to a low level, but the problem is to avoid the creation of a water pollution problem when the scrubber liquors are discharged. A scrubber system has been designed which eliminates discharge of aqueous effluents by recirculation of the scrubber liquors, with the exception of the effluent from the fluorine washer[37]. The system is illustrated in Fig. 1, as applied to a TVA-type process. 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 preneutralizer. 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.

It is claimed that the following performance figures are achievable with this system.

TABLE 3. 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

This system would require careful control in order to ensure that the operation of the scrubbers does not upset the water balance in the process, and some fertilizer manufacturers believe that this would create considerable difficulties. They also consider that the ammonia and dust emissions in Table 3 are low by a factor of at least 10 and are sceptical about whether they are achievable in practice.

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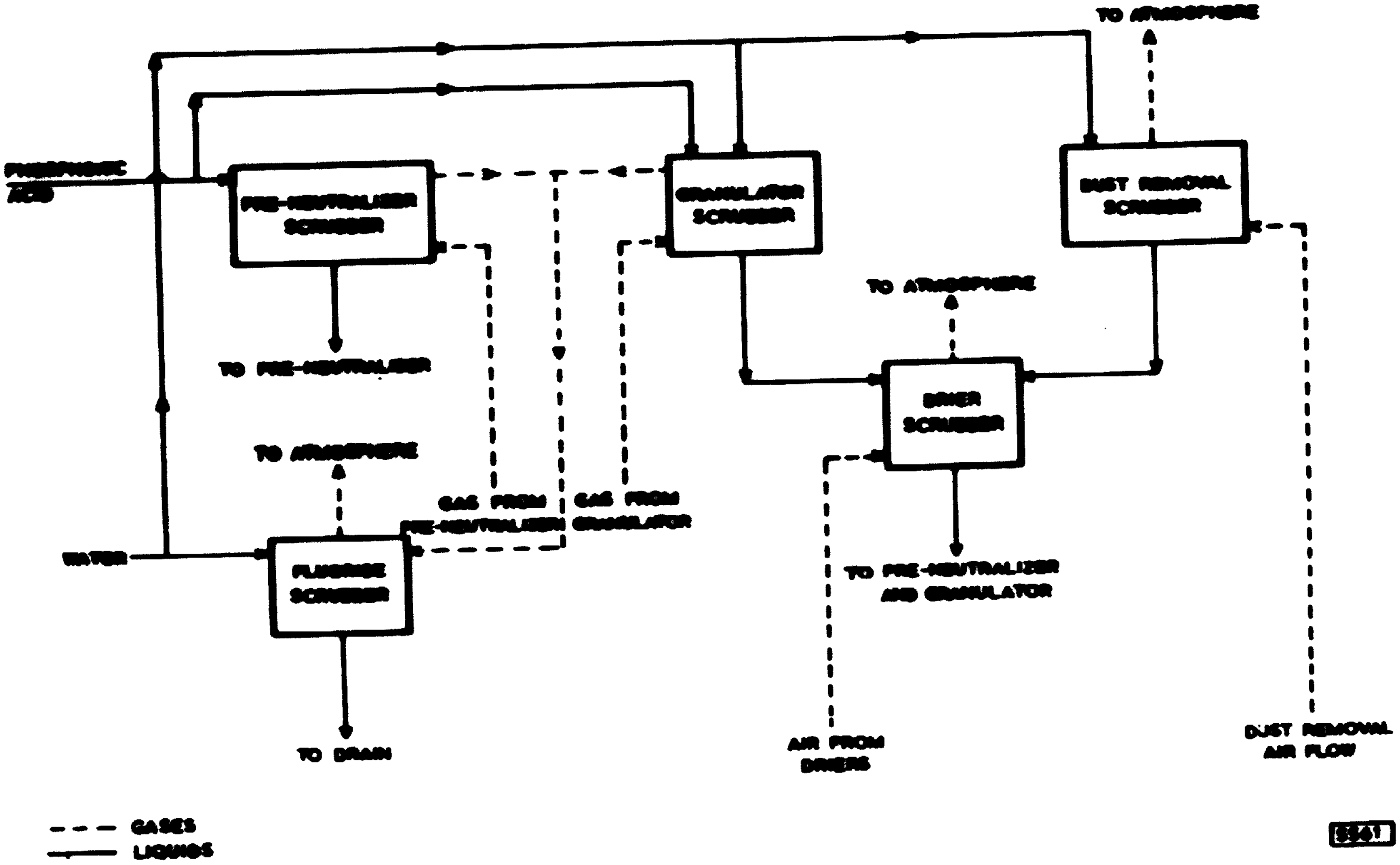
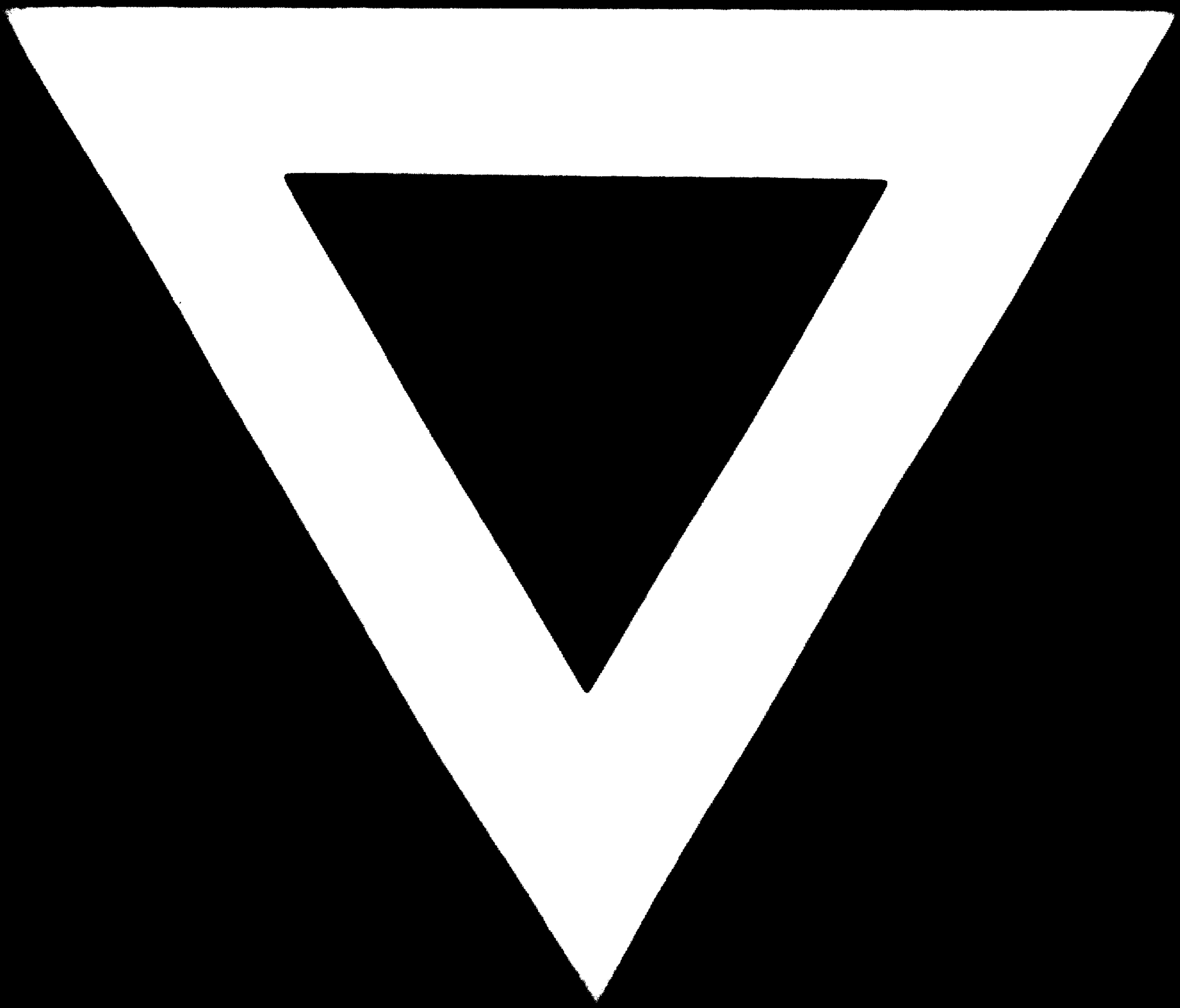


FIG-1 SCRUBBER SYSTEM FOR POLLUTION CONTROL IN A COMPOUND FERTILIZER PLANT

[redacted]



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