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ENVIRONMENTAL PROTECTION IN SULPHURIC ACID,
PHOSPHORIC ACID AND COMPLEX FERTILIZER PRODUCTION

By

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INTRODUCTION.

For several years, every ISMA Technical Conference has given us a number of papers dealing with environmental problems in connection with phosphoric acid or fertiliser plants (1). In most cases, the problems of disposal and control of effluent were studied from the point of view of the producing plant. To-day, we shall approach them from the point of view of an engineering company called upon to design, carry out and build the production units. It is a well-known fact that the battle against the various forms of pollution is a costly one, particularly when it is not provided for from the outset. The investigation of pollution problems, (like any other problem) at the design stage of units likely to cause pollution (and most of them are likely to do so to some extent) alone makes it possible to plan, calculate and optimise, whereas once the factory is built, any steps taken will of necessity be more expensive and in most cases not entirely adequate.

Furthermore, in the special cases of production plant for sulphuric acid, phosphoric acid and complex fertilisers, which we shall consider in more detail later, it is quite clear that it is not merely a matter of adding anti-pollution equipment to conventional production units, but that in the majority of cases engineers have to make radical changes to the design of the factory or even to the manufacturing process itself in order to obtain modern units which cause the minimum possible pollution.

NOTE : The authors would like to take this opportunity of thanking their colleagues at the Société Anonyme Heurtey, Messrs. H. Allyot and S. Thillard for their assistance in drafting the parts dealing with production units for phosphoric acid and complex fertilisers.

I PRODUCTION OF SULPHURIC ACID

In modern methods of sulphuric acid production by contact, effluents are few.

At the first stage, i.e. the production of gas rich in SO_2 , a distinction has to be made between units using pyrites (or other metallic sulphides) as raw material and those which use sulphur.

In the case of the calcination of pyrites, the gases resulting from the roasting must be completely freed from dust before being passed on to the catalyst unit; there are various systems which can be used (2), but, generally speaking, a wet scrubbing process is employed which produces a weak acid with a large dust content.

The disposal of this acid may be a problem unless there is a consumer unit, such as a superphosphate plant, near the installation.

In the burning of sulphur, there is no lethal waste; nevertheless, some precautions must be taken for storage, whether the sulphur be solid or liquid.

It is, however, in the second stage of sulphuric acid production units that the major problems of waste disposal arise. Whether the gas rich in SO_2 is prepared by roasting sulphides or burning sulphur, it must be converted into SO_3 (by catalysis) and then absorbed into the sulphuric acid. The residual gases discharged to the chimney will contain a quantity of SO_2 , SO_3 and sulphuric acid, depending on the type and efficiency of the catalyser and absorption installations.

At the present time, most operating units emit gases containing from 2 to 3000 ppm by volume of SO_2 and 3 to 5000 ppm of SO_3 in the form of vesicular SO_3 or sulphuric acid.

The amount of SO_2 and SO_3 discharged in this way into the atmosphere by plants installed in Western countries is estimated at over 5000 t.p.d.

What can be done to reduce, if not to eliminate, these emissions of SO_2 and SO_3 ?

First of all, let us recall the objectives recommended by the Environmental Protection Agency in December 1971 (3)

a) Limit of SO_2 waste

2 kg per metric ton of 100% sulphuric acid produced i.e. a catalysis efficiency of over 99.7%; for a unit working with 10% of SO_2 in the gases at the

converter input, this is equivalent to residual gases containing about 350 ppm of SO₂

b) Limit of vesicular acid waste

0.075 kg per metric ton of 100% sulphuric acid produced, i.e. about 15 ppm.

There are few ways of achieving these objectives :-

Residual gases may be processed to eliminate the SO₂ (and SO₃) usually by absorption ;

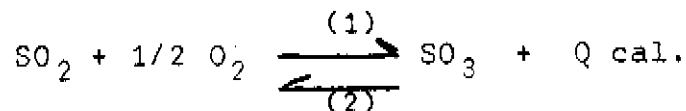
- or The catalysis and absorption processes must be improved so that only a very minute quantity of sulphurous or sulphuric gas is left in the effluent;
- or A combination of the two systems (in very special cases).

1. Absorption of the residual gases

This may be done by basic aqueous solutions and results in dilute solutions of a mixture of sulphite and sulphate, the disposal of which is often difficult and inconvenient. Apart from the high operating expenditure due largely to the cost of the reagents, it is often the case that atmospheric pollution is merely converted into liquid pollution (4).

2. Improvement of Catalysis Efficiency

The oxydation reaction of SO₂ into SO₃ is a reversible reaction, which may be written :



for which the equilibrium constant is given by :

$$K = \frac{(\text{SO}_3)^2}{(\text{SO}_2)^2 (\text{O}_2)}$$

Thus it is clearly possible to favour the reaction in direction 1 (formation of SO₃) by :

- a) increasing the pressure
- b) reducing the concentration of SO₃
- c) reducing the temperature

- a) in order to increase the catalytic pressure, it is necessary in practice for the entire sulphuric unit, including the burning of the sulphur, to operate under pressure. The increased output becomes worthwhile only if the operating pressure reaches or exceeds 4 to 5 bars. Owing, however, to the rise in the cost of the plant, a pressure of 8 to 10 bars would appear more rewarding (the increased volume on the apparatus would then compensate for the increased cost due to the greater thickness of metal required). Theory and calculation favour this type of unit. However, at the present time there is no industrial plant operating on this principle, either because the working costs (energy for compression) are too high or because the theoretical saving on investment does not counterbalance the risks involved in a new type of installation (5).
- b) In order to reduce SO_3 concentration it is advisable to eliminate the SO_3 formed in a first conversion period, in order to encourage the reaction of the SO_2 which has not been converted during the prior conversion period. This is the interabsorption process, also called "double catalysis".

The principle of interabsorption has long been well-known and a large number of patents have been filed on this subject in nearly every country in the world. (6) The basic principle of interabsorption is relatively simple (see Fig.1).

Gases rich in SO_2 pass through two or three catalyst beds in a conventional converter; they are then cooled and conveyed to an absorption tower where the SO_3 previously formed is absorbed by sulphuric acid. At the outlet of this absorption tower (called the interabsorption tower), they are heated to the starting temperature of the catalyst then pass again over a catalytic bed for the final conversion. In this last stage of catalysis, since the SO_3 concentration is very low, the overall conversion efficiency is improved. The gases are then conveyed (after cooling) to the final absorber.

As an example, if a conventional unit be compared with a unit using interabsorption, starting with an identical gas of 10% SO_2 - 11% oxygen, placing the interabsorption unit after three stages, so that at least 90% of the SO_2 has already been converted and, if in both cases the output temperature is 430°C ., the equilibrium calculation gives :

	<u>Conventional</u>	<u>Interabsorption</u>
Conversion efficiency	98.4%	99.85%
Residual SO ₂	1900 ppm	180 ppm

It may be observed that by increasing the conversion efficiency by less than 1.5%, the quantity of SO₂ rejected is divided by more than 10.

Comparable results are obtained in the case of gas derived from the roasting of sulphur with lower SO₂ concentrations.

- c) Lowering the temperature.
Conversion efficiency increases in proportion to the lowering of the temperature, but the catalytic reaction is effective only from a temperature related to the type of catalyst used. With a modern catalyst, this "starting" temperature can be reduced to 410 - 420°C., resulting in an output temperature at the final conversion stage of about 430°C.

At this temperature, for a catalytic charge of 160 to 180 litres per tonne H₂SO₄ p.d. and for a gas with 10% SO₂ at the input, the equilibrium is about 98%, giving the overall efficiency of a conventional unit.

In the case of a unit with double absorption, the gas at the output of the interabsorption tower is at approximately 0.8% SO₂; equilibrium is then obtained for about 96% of the converted, residual SO₂, i.e. an overall efficiency of 99.7%.

Thus, a limit is imposed by the operating temperature of the catalyst and, if a higher overall conversion is required, the rate of conversion in the first catalytic beds of the interabsorption must be increased. This is done, for example, by increasing the amount of catalyst used; in this way up to 99.9% conversion can be obtained.

3. Combination of increased catalytic efficiency and absorption of residual gases

The demands of environmental protection may create some very special cases and it is possible to reduce the concentration of SO₂ in the waste gases to 30 ppm by combining interabsorption and absorption of the residual gases in an alkaline solution. This would make it unnecessary to use up space on very large catalytic beds (which would be necessary to obtain more than 99.9% conversion) and would not require too much reagent (which would be necessary to absorb all the SO₂ from a conventional unit).

4. Reduction of the SO₃ waste and acid mist

When SO₃ is absorbed by sulphuric acid, acid mist is formed and this is carried along by the gases into the atmosphere unless adequate measures are taken to deal with them. The quantity of acid mist formed depends upon the temperature and the concentration of the wetting acid.

In order to reduce the formation of mist, an acid with 98 - 99% concentration must be used at temperatures ranging from 70 to 90°C.

If the concentration increases, (production of oleum) the amount of mist formed increases very rapidly. If the concentration decreases, absorption is very poor and SO₃ is found in the atmosphere.

The effect of temperature is also very important. If it is too cold, a thick cloud is formed (as in starting) ; if the temperature is too high the SO₃ vapour pressure increases and an appreciable amount passes into the atmosphere.

In order to satisfy the EPA recommendations, it is necessary to cut out virtually all mist created in the absorption towers. There are two effective means of doing this (collection of over 95% of particles greater than or equal to 1 micron)

- electrostatic filters
- BRINK type fog eliminators

The former are very bulky, difficult to install and to work, and their maintenance is tricky.

The latter are easily installed, require very little maintenance but create an additional loss of load in the systems (see Figs. IIa and IIb)

At the moment, the second system is used, and the latest measurements on industrial plant show that a figure of 15 ppm of vesicular acid can be achieved;

Note : It must not be forgotten that, in addition to the vesicular acid, there remains in the gas a quantity of SO₃ corresponding to the vapour pressure of the latter at the working temperature of the absorber.

II PRODUCTION OF WET PROCESS PHOSPHORIC ACID, GYPSUM PROCESSES AND CONCENTRATION UNITS

Effluents from these plants are made up basically of :-

- a) Dust from crude or ground phosphate emanating from handling and grinding systems .
- b) Vapour containing fluorine compounds resulting from the reaction of the phosphate and the concentration of the acid produced.
- c) Liquid acid from cleaning the plant and washing the vapour (which was discussed earlier).
- d) Solid gypsum resulting from phosphate attack and discharged from the filter.

It is useful to consult Slack's work (7) on the subject of treating these effluents.

1. Removing dust from phosphate handling and grinding systems.

The removal of dust from these systems makes it possible to limit the amount of P_2O_5 lost in the form of phosphate dust in the air. Such losses can be appreciable when the unit has not been designed for maximum recovery. The ground ore should always be handled and stocked in air-tight surroundings; air circulation to the atmosphere must be via dust filters. Air from the pneumatic handling system in the mills is also filtered before passing to the atmosphere. Such precautions will henceforth make it possible to limit the losses of P_2O_5 (by dust) to less than 0.1% by weight.

2. Treatment of vapours containing fluorine compounds.

Phosphate ore contains a large quantity of fluorine (3 to 4.5% by weight). A considerable amount of this (40 to 60%) is released in the form of gas during treatment of the rock and concentration of the acid.

The present anti-pollution standards no longer allow this fluorine to be discharged in gaseous form to the atmosphere or in dissolved form as liquid effluent.

Gaseous fluorine must be recovered in solution, precipitated and solidified. (8)

2.1 Release of fluorine during treatment of the rock;

1) Form in which fluorine is released.

Fluorine released during sulphuric attack on phosphate in the gypsum process is usually in the form of silicon tetrafluoride SiF_4 .

2) Quantity of fluorine released.

The quantity of fluorine released depends both upon the rock used and the process.

In the case of sulphuric attack on phosphate with precipitation of calcium sulphate as gypsum, the fluorine from the rock is distributed among three effluents, i.e:

acid produced,
precipitated gypsum
gas from the attack and the concentration

This distribution of fluorine depends upon the rock and the operations. However, the principal factors influencing this distribution are :-

- a) The sodium and potassium content of the rock; sodium and potassium having a tendency to precipitate fluorine in the form of fluosilicates or fluorine - aluminium - silica complexes, which go with the gypsum.
- b) The reaction temperature: the higher the reaction temperature, the more fluorine gets into the gas.
- c) The concentration of acid produced : the more concentrated the acid product, the greater is the quantity of fluorine released.

In general, for Morocco and Florida phosphates, the amount of fluorine released to the atmosphere is between 3 and 8% by weight of the fluorine from the rock, according to the process used.

3) The points at which vapour containing fluoric compounds is released in the manufacture of 30% acid.

These are fundamentally :

1. The reaction tank
2. The cooling system of the reaction tank
3. The first filtration section.
4. The filter vacuum system
5. The filtrate-collecting tanks

Most vapour is generated at the reaction tank and its cooling system; this must be treated.

However, in order to satisfy modern anti-pollution standards, it is also essential to deal with vapour from the first filtration section, and, if necessary, vapour from the first filtrate-collecting tanks (30% acid).

Gases from the filter vacuum system are also treated and this, in addition to limiting atmospheric pollution, makes it possible to use vacuum pumps made of modern materials.

4) Treating gaseous effluents

As we have already mentioned, gaseous effluents are washed and the liquid resulting from the washing forms either a commercial product (aqueous solution of fluosilicic acid) or a liquid waste which could create pollution and must be treated before discharge.

In washing the reaction gases, the silicon tetrafluoride is absorbed by the water and gives an aqueous solution of fluosilicic acid, while the silica is precipitated.

If the washing temperature is below 50°C, silica is precipitated in gelatinous form; at a higher temperature the silica is precipitated in the form of hard granules which may be cemented to each other.

Encrusting is therefore a serious problem in the washing of effluents from a reactor in a phosphoric acid production plant.

Methods of gas washing in current use make it possible to limit the amount of fluorine discharged into the atmosphere to less than 50kg p.d. for units producing 800 t.p.d. In order to obtain such low figures it is essential to treat all gaseous effluents.

Fluorine content of the principal gaseous currents:

gas from the reaction, with a vacuum cooler:	300/1000 mg/Nm ³
gas from the reaction, without vacuum cooler :	200/700 mg/Nm ³
gas from first filter sector :	100/200 mg/Nm ³
gas from strong filtrate collecting tank :	50/100 mg/Nm ³

From the point of view of washing, it would seem that a reaction system containing a vacuum cooler is better because the amount of gas to be processed is smaller and hence its fluorine content much greater, since the quantity of fluorine to be eliminated is substantially the same.

The varying compositions of gases to be treated clearly shows the economy of using a multi-stage treatment so as to wash the maximum of fluorine at maximal partial pressure, and to wash all gases with a comparable fluorine content together.

5) Choice of type of washing apparatus

Two considerations govern the choice of washing apparatus :

- a) A washing unit recovering a large quantity of fluorine must be capable of carrying crystalline silica.
- b) A unit washing gases discharged into the atmosphere must be of the highest possible efficiency.

6) The Washing Operation.

At the present time, good gas-washing is carried out by two units in series.

The first washing unit of moderate efficiency capable of carrying silica treats the gases from the reaction bath; This washer may be a vacuum atomising column, a cyclone washer or a Venturi washer.

A second high-efficiency unit, placed below the first, treats the gases from the first unit together with other polluted gases such as those from the filtration unit and from the first filtrate tank.

This washing unit is in general highly efficient. The composition and quantity of the spraying liquid is such that silica is not precipitated.

2.2 Release of fluorine during concentration of acid:

During concentration of phosphoric acid from 30% to 54% by weight P_2O_5 , 30 to 40% by weight of fluorine from the rock is released into the resultant vapour.

In a plant for concentration by submerged combustion, the fluorine is mixed with non-condensable gases which have to be washed in systems similar to those described for washing the gases of a plant producing 30% acid.

In the case of a vacuum concentration plant, the fluorine is absorbed by the water of barometric condensers. However, in some cases it may be found economical to recover the fluorine in the form of a commercial solution of fluosilicic acid, titrating at up to 22% by weight of H_2SiF_6 .

It will be observed that in the case of an immersed-combustion concentration plant, the dilution of the fluorinated compounds in the combustion gas makes a process of fluorine recovery by washing economically difficult in practice.

- 1) Form in which fluorine is released during the concentration of phosphoric acid.

Fluorine is released in the form of a mixture of HF and SiF_4 ; the molar ratio HF: SiF_4 depends upon the P_2O_5 content of the acid and upon its origin (substantially upon the SiO_2 content of the acid); thus, for an acid derived from a Florida phosphate, this ratio is less than 2 for P_2O_5 concentrations below 50%, substantially equal to 2 for P_2O_5 concentrations between 50 and 56% and greater than 2 for P_2O_5 concentrations higher than 56%.

- 2) Recovery of fluosilicic acid.

For this purpose a fluorine washing unit is placed between the flash chamber of the concentrator and the barometric condenser.

The washing liquid consists of a solution of fluosilicic acid, whose concentration may go to 22% by weight of H_2SiF_6 .

The type of washing unit in general use is a vacuum tower with spraying racks:

- 3) Quantity of fluorine recovered by washing : efficiency of washing units

The quantity of fluorine recovered depends upon :

- a) the washing temperature and therefore the working pressure: the lower the washing temperature, i.e. the working pressure, the greater the recovery.

- b) the concentration of the washing solution of fluosilicic acid: the lower the concentration of this solution, the greater the recovery.
- c) the fluorine content of the vapour undergoing washing: the higher the fluorine content, the greater the recovery.

Example of washing efficiency as a function of the pressure and concentration of the washing liquid with concentration of a phosphoric acid from 30% to 54% by weight with a single evaporation stage :

PRESSURE	mm Hg	65	38	65
TEMPERATURE	°C	39	32	39
CONCENTRATION OF THE ACID PRODUCED (% H_2SiF_6)		25	25	15
MAXIMUM WASHING EFFICIENCY		80%	90%	93%

4) Practical Operation.

a) Single stage concentration :

In the concentration of phosphoric acid from 30 to 54% P_2O_5 , the fluorine is released in the form of $HF + SiF_4$ in such a way that the mixture in solution is practically fluosilicic acid.

On the other hand, the concentration of phosphoric acid from 30 to 45% releases a greater part of fluorine in the form of SiF_4 so that, in the washing liquid, H_2SiF_6 in solution and a gelatinous precipitate of SiO_2 are present.

In this case, the fluorine washing plant must be provided with a system of filtration for the fluosilicic acid which will eliminate the precipitated silica. This filtration is usually effected on underlay filters (diatomic earth forming the underlay) and under pressure.

The plant should be cleaned periodically in order to eliminate silica deposits.

b) Multi-stage concentration in series
(2 or 3 stages)

In this case, each of the concentration elements works at a different P_2O_5 level: for example, in order to concentrate from 20% to 54%; the offtake at the various elements are approximately as follows :

	<u>2 elements</u>	<u>3 elements</u>
Supply	30	30 (% P_2O_5)
Output 1st element	43	37
Output 2nd element	54	45
Output 3rd element		54

The vapour given off at each of the elements are at different pressures and have different compositions.

Separate washings of the vapour from the first two elements result in fluosilicic acid solutions containing precipitated silica, the washing of the last element results in a solution of HF and H_2SiF_6 . However, the mixture of these solutions constitutes a solution of fluosilicic acid containing practically no free silica and no free HF.

In order to minimize problems arising from silica deposits in the washing systems of the first two elements and problems of corrosion from HF in the washing unit of the third element, it is essential to mix the various washing acids.

This is detrimental to washing efficiency.

One way of overcoming this defect is to reduce the working pressure of the washing units of the first and second elements and to bring it to the level of that of the third element; the efficiency thus gained is considerable but is detrimental to the amount of cooling water carried onto the barometric condensers of the elements modified in this way.

In short, with only one washing unit on each evaporation element, it is impossible to reconcile high level of recovery and consequent low pollution with high content of fluosilicic acid produced.

For a fluosilicic acid titrating at 22% by weight of H_2SiF_6 for a concentration system with three elements in series the recovery efficiency is between 60 and 70%.

The high recovery levels of the fluorine contained in the vapours of the vacuum concentration units can only be obtained by putting washing units in series on each element.

In present day working installations, fluorine is recovered for commercial purposes; a single washing unit is used and 30 to 40% of the fluorine from the acid, i.e. 10 to 15% of the fluorine in the rock, passes in soluble form into one of the barometric condensers.

3: Disposal of gypsum

3.1 The disposal of the gypsum produced by a phosphoric plant is, together with fluorine pollution, a vital problem.

According to the P_2O_5 content in the rock, the quantity of gypsum per ton of P_2O_5 produced is between 4.4 and 5.3 tons, which, for a plant of the order of 500 t.p.d. represents an average production of 2,500 tons of gypsum each day.

Such quantities of solid matter can no longer be thrown into waterways or into the sea: It is at least necessary, if this gypsum is to be thrown into the sea, to dispose of it in suspension (20% by weight of solid matter), which can be pumped and discharged by pipeline into a current which will carry it well out to sea.

The gypsum is then dissolved in the sea-water:

(solubility of gypsum in fresh water : 2.3 gr/litre
solubility of gypsum in sea water : 3.5 gr/litre)

However, not all P_2O_5 manufacturing plants are near the sea. In the U.S.A. a well-known method of disposal of gypsum is to pile it in tips or spoil-heaps.

The gypsum, repulped to 15/20% solid substances, is pumped to a dumping ground. The clarified water is recovered and used to transport the gypsum.

This process requires a large area (2,200 sq. metres per ton P_2O_5 produced each day). Moreover, the water carrying the gypsum is saturated with fluorine and contains a large quantity of P_2O_5 .

The gypsum-dumping and water-recovery areas must be surrounded by dykes to prevent water seepage.

Where the cost of land is high, dykes can be used to raise the level of the area; but then mechanical means must be used to handle the gypsum and the pumping cost increases: dykes 20 to 30 metres high are in use. Where a plant is erected at the mine site, old opencast workings can be used for dumping.

Water recovery :

When the gypsum is handled in repulped form, one important aspect of the problem is recovery and cooling of the gypsum-repulping water. Except in very special cases, it is in fact impossible to use the water once only.

Among the recommended solutions it is necessary to make a distinction between the disposal of the repulping water and of the water from the barometric condensers in the same circuit, and separation of the circuits.

The latter solution has the advantage of greater flexibility and better land utilisation.

Several plants employ cooling circuits provided with a section for treatment of the water with lime for defluorisation, but the ratio of lime necessary for this is high (300 kg of CaO per ton P₂O₅ produced).

In order to limit the consumption of lime, one solution is not to treat all the water in the circuit but to treat only that part of the circuit designed to trap the solid matter so that the waste water conforms to anti-pollution standards.

3.2 Valorisation of the gypsum by-product.

The cost of disposal of gypsum at sea is high and represents a squandering of natural resources. Any economically viable process which enables gypsum to be used as the basis of any form of manufacture is therefore of interest.

The principal solutions considered in this respect were :

- the manufacture of plaster and cement
- the manufacture of ammonium sulphate
- the manufacture of sulphuric acid which would be re-used in the phosphoric unit with resultant savings in raw material consumption.

Unfortunately, these various processes have hitherto been used only in very special economic conditions, but new ideas which are emerging on the conservation of natural resources may induce industry to look at the whole question in a completely new light.

This paper is already rather long and we do not wish to overburden it by describing these various processes, but we would refer those who are interested to a number of works or articles where they are described in detail .(9)

III TREATMENT OF EFFLUENT FROM A COMPLEX FERTILISER FACTORY

1. Introduction.

One of the characteristics of complex or compound fertiliser manufacture is the use of materials in very different forms : solids, slurry, liquids, gases : this makes the methods necessary to combat pollution and to protect the environment very complex. The reduction of solid, liquid, or gaseous effluent waste does, however, tend to reduce the loss of raw materials and thus to improve the yield of the plant.

The solid effluents are fertiliser dusts. These dusts are recovered either by dry or by wet cleaning. The gaseous effluents are in particular NO_2 , NH_3 and fluorine in the form of HF or SiF_4 . These gases are absorbed in washing units. The liquid effluents contain dissolved fertilisers, fluorine from the process itself, or from the washers mentioned above. Liquid effluents have either to be recycled in the process or treated.

Our Company has two types of complex fertiliser factory :

- a) "Nitric attack" plants in which phosphate rock is attacked by nitric or phosphonitric acid, and the resultant slurry prilled after separation of the calcium nitrate, neutralisation with ammonia, evaporation and mixture with potash.

The principal effluents from these factories are :

- Ca^{++} ions given off either in the form of calcium nitrate or of calcium sulphate if sulphuric acid or ammonium sulphate are added.
- gases escaping from the reaction and neutralisation tanks (F , NH_3 , NO_2).
- dust from the handling of solid products.

The problem of control and treatment of effluent is substantially the same for this type of factory as for the type referred to in b) and used to illustrate the description. It is the same problem in the sense that the two types of process produce complex gaseous effluents loaded with dust. Gas and dust are picked up either dry, or during the washing process, carrying liquid products to be reintegrated in the unit.

- b) "TVA"-type plants intended to produce rich formulae such as 17-17-17, 15-20-20, 30-10-10, 24-24-0 and consisting mainly of the following unit

1. A preneutraliser in which the liquid ammonium nitrate, phosphoric acid and gaseous NH_3 are mixed.
 2. A rotary drum, known as an "ammoniator-granulator" in which the "slurry" from the preneutraliser, the recycled potash, any ballast and the ammonia intended to complete the ammoniation of the product fall by gravity.
 3. The principal dryer followed by a screening section and a grinding section.
 4. A finishing sequence, including the final cooler and the coating unit.
2. Points at which pollutant dust and gases are emitted.

2.1 Preneutraliser

For the formulae mentioned above, the preneutraliser operates at temperatures between 140°C and 150°C . The presence of nitrate in the preneutraliser liquidizes the slurry and makes it possible to work at low water concentrations, resulting in a reduction of the recycling rate. At these temperatures the vapour pressure of the ammonia above the solution is fairly high even when one does not exceed the molar ratio $\text{NH}_3/\text{H}_3\text{PO}_4 = 1.45$ and quantities of ammonia escape from the slurry, comprising between 8 and 12% of the total quantity introduced into the preneutraliser. Efficient washing of the gases made up of water vapour (1.8 Kg per Kg of NH_3 introduced) of NH_3 and fluorine is therefore necessary.

Above the slurry only small quantities of fluorine are released. On the other hand, during the washing with phosphoric acid of the ammonia from the preneutraliser, this acid is brought to a high temperature, resulting in the release of fluorine in the washing unit.

Measurements have shown that the quantity of fluorine present in the gases at the output of the washing unit of the preneutraliser amounted to between 0.4 and 4 Kg per ton of P_2O_5 . This figure varies according to the characteristics of the acid (origin of the phosphate, concentration) and its temperature. For a production of 1000 t.p.d. of 17-17-17, the figure of 4 Kg per ton of P_2O_5 corresponds to an amount of 680 Kg p.d. of fluorine waste.

2.2 Granulator

Air circulates through the granulator at negative pressure, the air-flow being adjusted to the requirements of the granulation.

At the output this air contains moisture, fertiliser dust and that part of the NH_3 introduced into the granulator which has not been fixed.

Ammonia losses increase with the increase of the molar ratio $\text{NH}_3/\text{H}_3\text{PO}_4$ desired in the product; they may reach up to 15% of the NH_3 introduced in the granulator, if the molar ratio be high (> 1.85). In view of this, it is preferable to inject liquid ammonia into the granulator and it is important to design injectors which dig deeply enough into the granule bed.

The quantities of fluorine released are very small.

2.3 Dryer.

The main effluent from the drier is fertiliser dust in amounts varying with the humidity, granulometry and formula. Most dust particles are between 50 and 500

2.4 Miscellaneous.

2.4.1. The final cooler is of the type with fluidised bed. Since the product is calibrated and does not roll about loosely only very small quantities of dust escape.

2.4.2. The dust from the cleansing circuit is fine and therefore difficult to collect.

2.4.3. Fertiliser manufacturers are well aware that it is essential to maintain in good order with a high standard of cleanliness the following parts of a fertiliser plant :

- screens
- vibrating conveyers
- conveyor belts
- feet and heads of skip hoists
- grinders and mills
- coating units

It is considered that the dust content in the atmosphere of a fertiliser factory should not exceed 15 mg/m^3 and one way of doing this is by keeping potentially dust producing units in vacuum.

3. Methods of dust recovery and effluent washing in general use.

All modern fertiliser plants now use batteries of "high efficiency" multicyclones on dust producing units. Yields from collection are usually as follows :-

particles	$< 2.5 \mu$	68%
particles	$< 5 \mu$	85%
particles	$< 10 \mu$	95%
particles	$< 25 \mu$	99%

Total yields differ according to the granulometry of the dust; they are usually between 94% and 98.5%. Each cyclone can treat up to 20,000 m³/hour of gas with a P of 100 to 120 mm CE.

Dust-collecting hoppers under the cyclones are provided either with rotary cellular traps or rubber sleeves kept closed by vacuum and automatically opening when the weight of dust collected becomes sufficient. The T.V.A. have experimented with "wet collection systems": the dust falls directly into a trap where flowing water dissolves the fertiliser particles.

Sleeve filters, which are much more efficient, are sometimes used instead of cyclones. Unfortunately they have the following disadvantages:

- very bulky
- low heat resistance
- it is necessary to provide for reheating after stopping
- dirty, resulting in an increasing loss of throughput as time goes on
- no collection of gaseous effluents
- very expensive

They are therefore used only for very fine products, such as : cleaning the hoppers with talc or ground phosphate.

The cyclones are most frequently followed by wet washers meant to pick up the finest particles which would not be held, or only partially so by the cyclones. These fine particles consist of dust of a diameter of less than 10 microns and may also be the "smoke" of ammonium chloride.

Ammonium chloride is formed either by the action of sulphuric acid upon potassium chloride (formation of hydrochloric gas, then ammonium chloride) or by displacement between the ammonium salts and potassium chloride; this "smoke" is released only from a temperature of the order of 150°C. It may therefore appear particularly in the dryer when heated to temperatures higher than 150°C (which does not apply in the case of the formulae referred to above) or in the granulator, when sulphuric acid is conveyed to it. **It is very difficult to filter out**, even in wet washers.

The following are the principal wet-washing devices :

- Spray system.
Dust collection is effected by contact between dust and water droplets. Washing efficiency depends mainly and increasingly upon the relative speed between droplets and particles, upon the diameter and upon the number of droplets. There are gravity spray towers (free-falling water droplets), towers in which mechanical or pressurised spraying enables high dispersion and high speed to be attained, venturi scrubbers in which the injection of water at the neck of the venturi carrying the gas at high speed results in excellent dispersion and a high speed gradient. The efficiency of the spray systems also depends upon other factors such as diffusion and condensation.
- Impingement scrubbers
In these washers the incoming gas collides violently with the surface of the washing liquid. The particles are retained in the liquid while the gas is deflected.
- Packed towers
These are used very widely in the fertiliser industry. At the present time there are spray towers including one or two layers of polypropylene spheres. The latter are free to move between two grids under the action of the gas current and allow good contact between gas and liquid.

The types of apparatus described above operate also as absorbers of the polluting gaseous effluents (NH_3 and F) which may be emitted with the dust. Generally speaking they are followed by cyclonic-droplet recuperators.

Above the reactors, from which no dust escapes but only water vapour and gases, "spray towers" are usually placed (empty or packed). Absorption is effected by the washing liquor whether or not recirculated.

The factors influencing choice among the various types of washer should include :

- efficiency
- Δp gas
- water consumption
- easy cleaning and resistance to fouling
- costs of operation and investment

4. Washing system employed in the HEURTEY units.

Many combinations of washing systems may be used and we shall now describe a typical lay-out which has proved highly efficient in various industrial concerns. (see Fig. III)

- 4.1 Most of the phosphoric acid consumed in the unit is recirculated via the washer of the preneutraliser before going into the preneutraliser. This washer is an empty cylinder provided with several spraying racks and the acid is projected in diametric planes. The input of the gas is tangential, making possible a primary cycloning of the droplets. The washer is provided with a devesicular cylinder of smaller diameter intended to recover on its inside wall the droplets centrifuged by a static propeller situated at the head of the devesicator.

Ammonia recovery is excellent and washing efficiency of the order of 99%. The gas is less than 20 mm CE.

- 4.2 The gases from the dryers and the ventilation system of the plant pass into high-efficiency cyclones. The dust is recovered and brought to the head of the granulator. Hoppers under the cyclones are equipped with scraper chains and rubber extraction sleeves.
- 4.3 Gases from the granulator do not pass into a cyclone (which would be very quickly blocked due to their high steam content) but go straight into a washer of the same type as that of the preneutraliser.

Fresh water and acid go directly into the recirculating tank of this washer. The molar ratio of the washing solution is kept at 1.3. If the molar ratio is between 0.8 and 1.3, there is a risk of crystallisation. If the molar ratio should be below 0.8 there is still a risk of crystallisation in the event of abnormal NH_3 losses in the granulator and of an increase in the molecular ratio. It would also seem that atomisation is less fine and less efficient, since the viscosity of the solution is higher for a solution containing a larger quantity of phosphoric acid.

- 4.4 The overflow washing solution from the washer of the granulator runs into the recirculating tank of the washers of the dryers and of the cleansing washer.

These washers are of the "fluoliquid suspension" type. The gases pass into a vertical diffuser into which the washing liquid is injected.

The liquid is atomised into fine droplets which remain in suspension (their weight is equal to the drag force exerted by the gaseous current). In order to have suspension, the diameter of the drops may not be as small as in a venturi scrubber and therefore the principle on which the device operates is different.

With this type of washer, no great difference of velocity between particles and droplets is sought. The important point is the phenomenon of diffusion with absorption. In the presence of soluble and easily moistened dust, efficiency is over 99% for dust particles emerging from an efficient multicyclone and having in practice a particle size of less than 15 microns.

Since this type of washer is virtually at saturation point because of the thermal heat exchange due to the continuous deformation of the liquid droplets and the turbulent mixture which occurs, there may also be condensation around very fine particles, which increases dusting efficiency still further.

This type of washer also gives a good performance in the absorption of the gases by liquid, and this again is doubtless due to the great turbulence and constant renewal of the surface of the droplets. The small quantities of NH_3 and fluorine which escape from the dryer are therefore collected by the washing liquor.

Recovery of the droplets is effected at the top of the diffuser after the gases have passed through a static propeller which centrifuges them.

The Δp of the washers is 150 mm CE.

After circulating in the "fluoliquid suspension" washers, the liquid is conveyed to the preneutraliser in order to check its temperature and sometimes to the granulator for the requirements of granulation. Nothing is drained away and there is, therefore, no loss of the raw material which has been recovered in the washers. The regulation of the supply of fresh water entering the unit is effected by checking the level of the circulating tank of the washers, of the driers and of the cleansing plant.

- 4.5 The gases from the washer of the preneutraliser pass through a defluorinating washer of a type similar to the washer of the preneutraliser or the granulator. Efficiency is above 95% with a large outflow of non-recirculated water.

It is also possible to provide for recirculation of the washing liquid. Efficiency will be slightly lower, but the quantity of water leaving the washer will obviously be reduced (a recycling rate of 1.5 is admissible) and may easily be added either to the far greater effluent from a phosphoric acid unit or treated with lime and returned to the washer.

Comments on the washing system.

The following were the reasons for selecting this system:

The NH_3 - losses from the preneutraliser are considerable for formulae of this type. It is advisable to treat the effluents from the preneutraliser and the granulator separately. The air-flow through the granulator may be high for some formulae and ammonia recovery becomes more difficult if it is diluted in a great deal of air.

Since the preneutraliser is fed with concentrated acid, it is possible to add a maximum amount of water separately. This water first of all flows into the circuits of the washer of the granulator, then of the dryer washers and the cleanser washers. Thus the unit is operating at maximum density in those parts of the system most full of dissolved dust and, to that extent, risks of clogging are minimised. There is always a minimum of water and this prevents waste flowing to the drains.

Provided that the preneutraliser is running steadily and the walls of the washer are well irrigated, the use of concentrated phosphoric acid for washing the gases from the preneutraliser entails no disadvantages and allows highly efficient washing, since the molar ratio of the washing solution is very low.

The washers of the dryers and of the cleansing circuit have a high evaporating capacity. Thermal exchange is highly efficient and the heat supplied by the air evaporates a not inconsiderable amount of water which has to be returned to the circuit in the form of fresh water.

This water flows first into the washer of the granulator, thereby reducing by that amount the density of the washing solution circulating in the washer. It then arrives as "make-up" water in the flow circuit of the washers of the dryers and of the cleansing plant. After these washers, i.e. where the density is highest, the quantity (q) of charged liquid is extracted which is required to maintain the temperature of the preneutraliser and to be transferred to the granulator. For a given quantity (q) and a given weight of dust collected in the washers, the density of the liquor recirculated to the washers is lower when the make-up water is stronger and therefore evaporation in the washers is greatest.

5. Cleansing.

The cleansing plant must ensure the collection of dust, the extraction of the cleansing gases and evacuation after cycloning and wet washing. The units emitting the

largest quantity of dust are undoubtedly the vibrating conveyor belt feeding the screens, the screens themselves and the coating unit when there is poor adjustment of the talc output. (It is wise to ensure that the flow of coating is adjusted to the flow of fertiliser into the coating unit).

Each cleansing intake is provided with a guillotine regulator and an adjustable air intake ensuring the correct rate of flow through the apparatus and ensuring the correct speed for the dust-laden air through the piping of the cleansing system. This speed must be between 20 and 25m/sec. The pipes must be as short and steep as possible. The draught through the ventilator for a unit of 1000 t.p.d. is 50,000 m³/hour.

6. Conclusion.

Modern technology has made it possible to equip fertiliser units with apparatus capable of reducing the discharge of pollutant effluent to a minimum.

The amount of dust discharged into the atmosphere is practically nil. The amount of NH₃ and F escaping to the atmosphere is small because of highly efficient washing devices. Finally, no liquid effluent is discharged into drainage systems.

It has been estimated that the cost of a washing installation in a unit of 1000 t.p.d. represents 11% of the cost of the capital equipment. Apart from the fluorine washer, the units are quickly written-off.

For example, for an output of 1000 t.p.d. of 17-17-17, the amount of ammonia escaping from the preneutraliser is 250 kg/hour. Assuming the efficiency of the washer to be 99%, and a cost price of 200 francs for one ton of NH₃, we recover :

$$0.99 \times 0.250 \times 8\ 000 \times 200 = 396,000 \text{ francs per annum}$$

The quantity of NH₃ escaping from the granulator may reach 70 kg/hour. Therefore about 105,000 francs per annum is recovered, assuming the efficiency of this washer to be less than that of the preneutraliser.

The quantity of dust escaping from the equipment may be assumed to be 2000 Kg/hour for a unit of 1000 t.p.d. Taking as a basis a cost of 240 francs per ton of fertiliser and assuming the efficiency of the cyclones to be 95% and that of the washers after cyclones 99%,

it is clear that we recover :

0.95 x 2 x 8 000 x 240 = 3 648 000 francs with the
cyclones

0.99 x 0.1 x 8 000 x 240 = 190 000 francs with the
washers after cyclones

The saving achieved by wet washing is less apparent;
from now on, however, it will respond to the requirements
of environmental protection and the control of noxious
substances.

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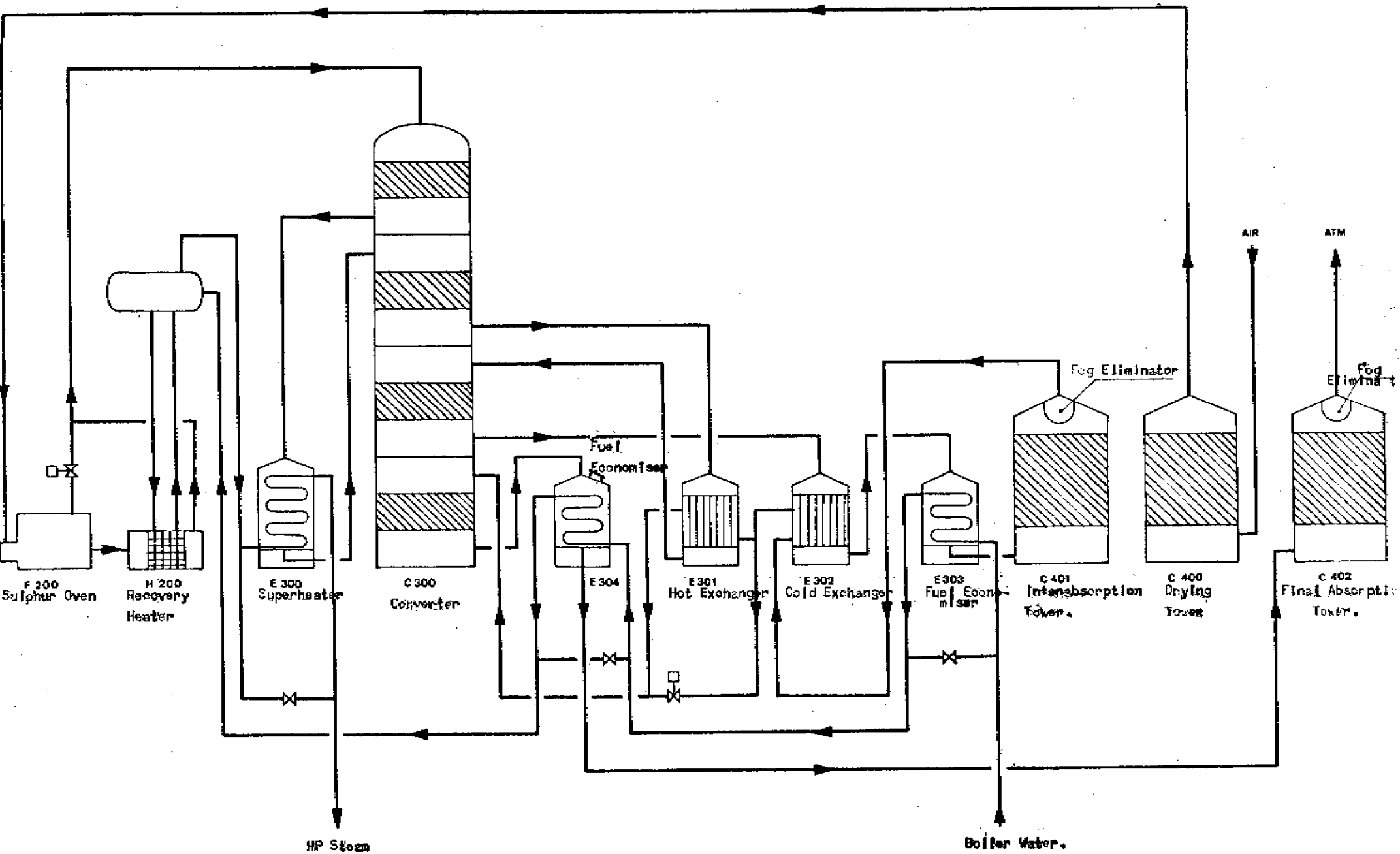


FIG 1: LAY-OUT OF H_2SO_4 PLANT WITH INTERABSORPTION

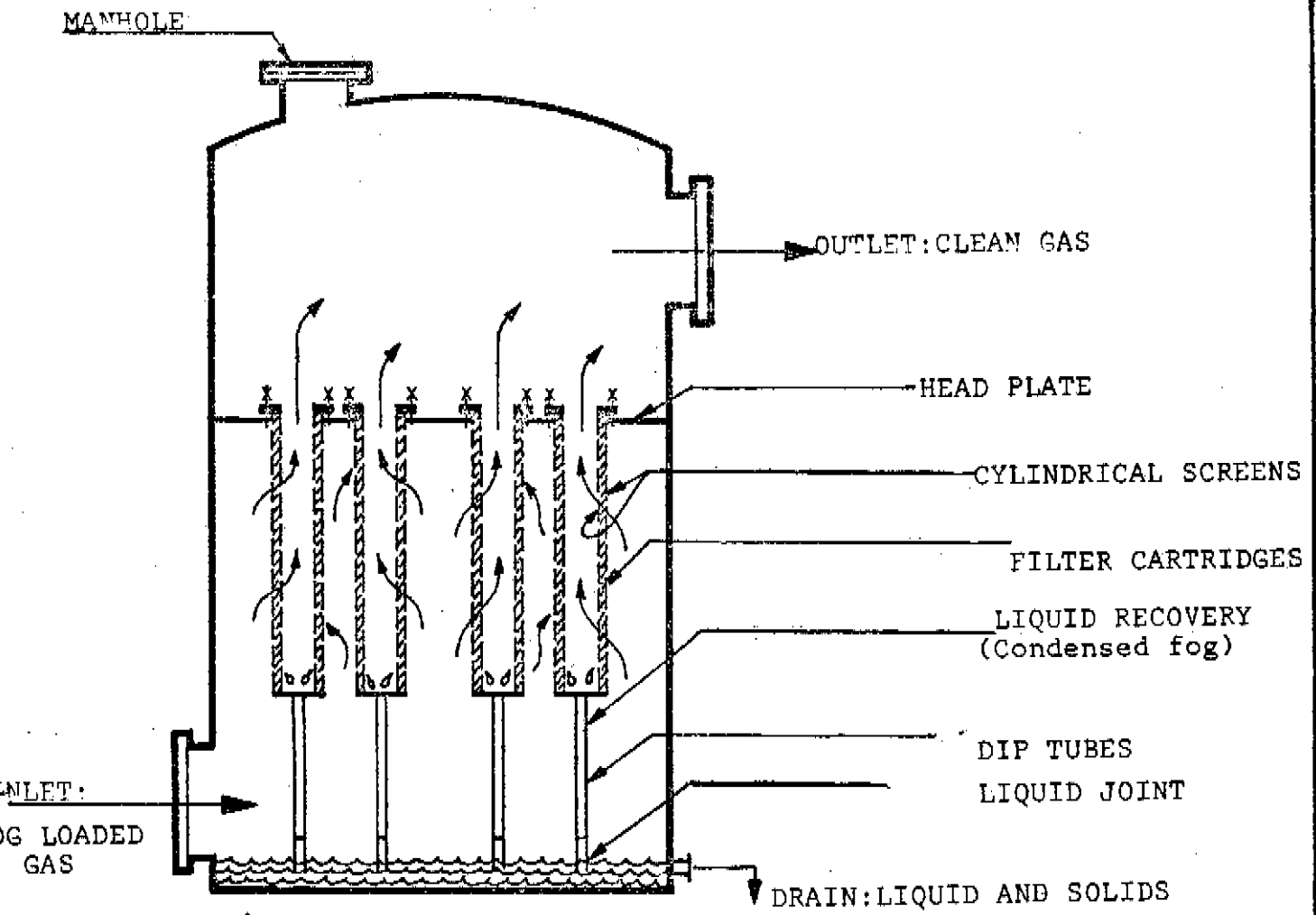


FIGURE II A

LAY-OUT OF BRINK ANTI-FOG SYSTEM, TYPE H-E

WITH MULTIPLE ELEMENTS.

TYPE H-E

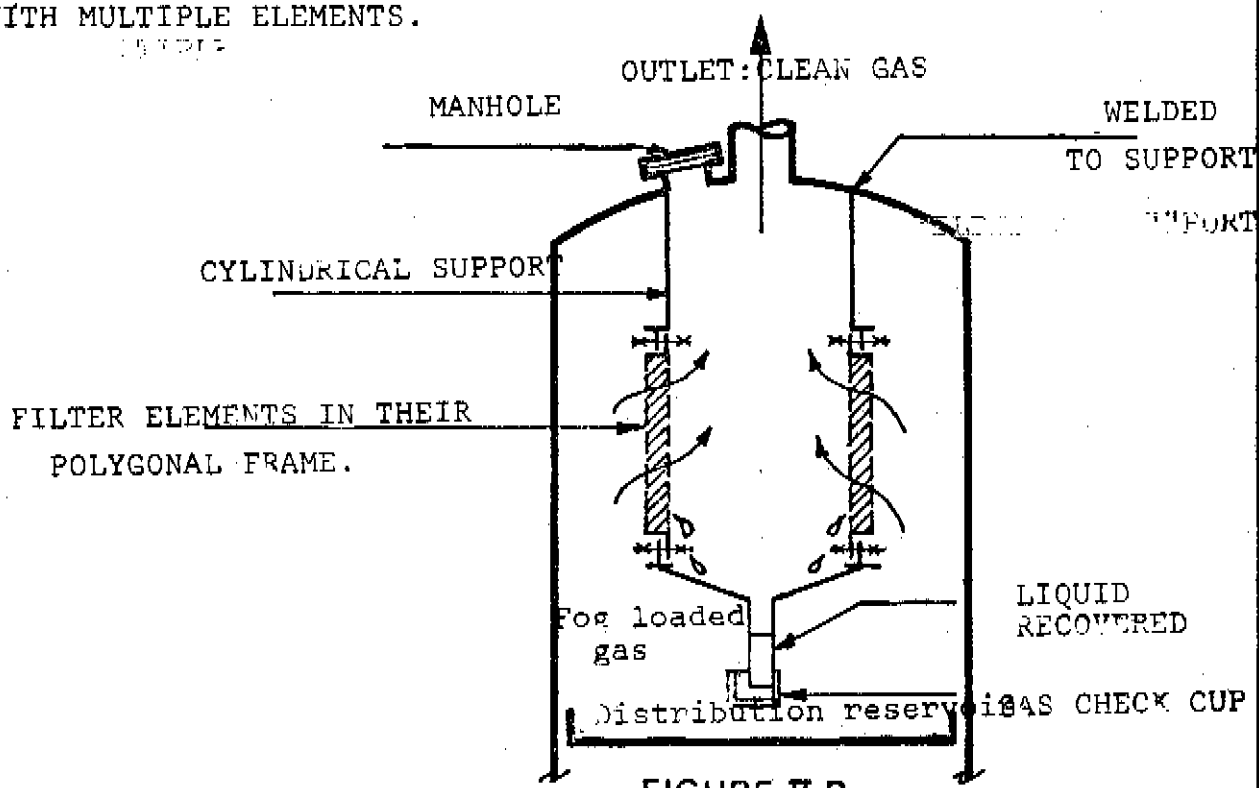


FIGURE II B

LAY-CUT OF BRINK FOG ELIMINATOR, TYPE H-V.

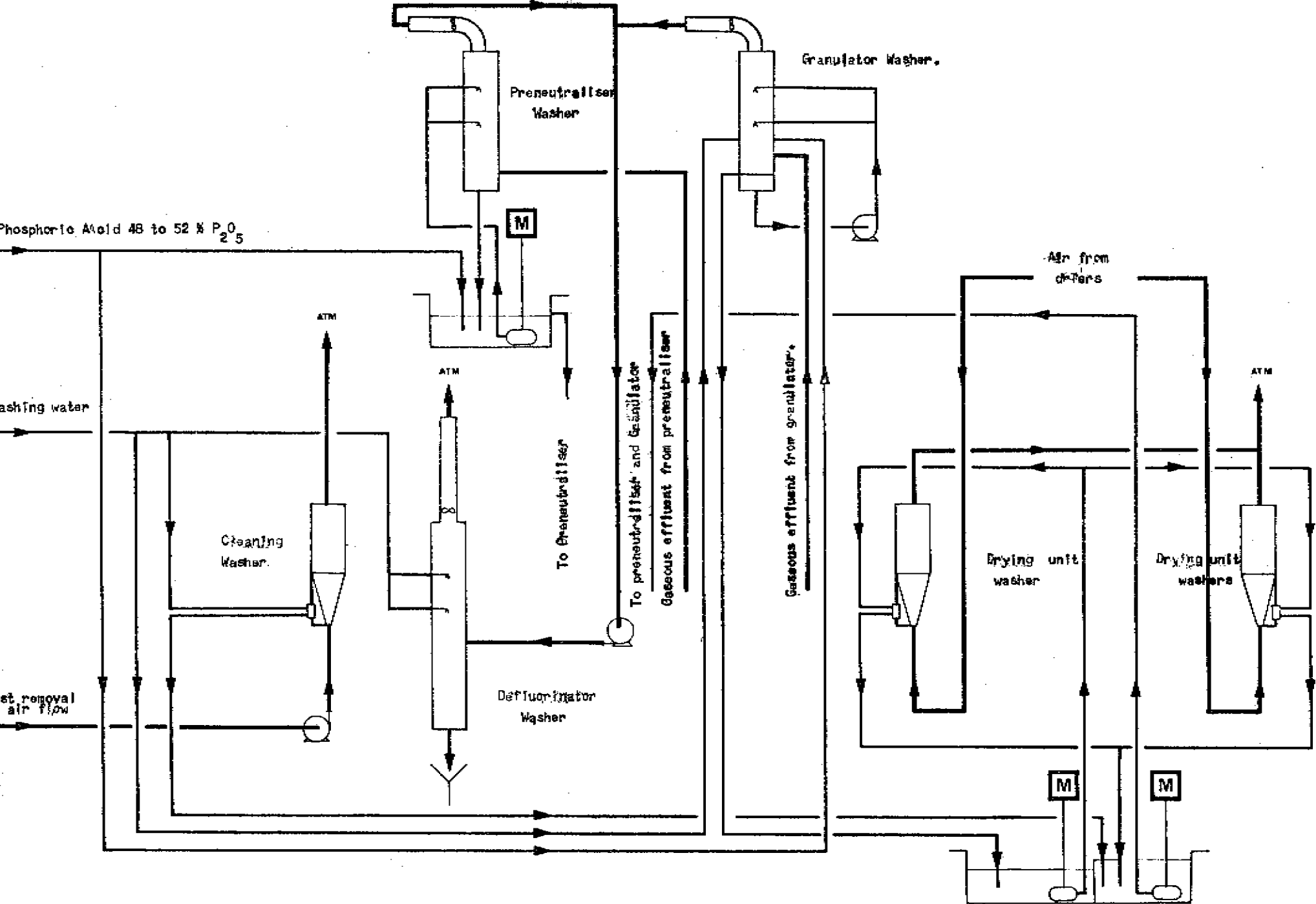


FIG III: NPK FERTILIZER PLANT: WASHING LAY-OUT