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MINIMIZING POLLUTION FROM PHOSPHATE FERTILIZER PLANTS INCLUDING CAPTIVE ACID PLANTS[1]

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INTRODUCTION

Environmental pollution control is a problem common to several branches of science. We should also remember that it is a global problem, because individual nations do not own the oceans and the air knows no boundaries.

In the production of both phosphate fertilizers and the acids (sulphuric, nitric and phosphoric, for example) used in producing them, substances are released which are harmful to the environment, i.e. they may do harm to plants, animals (fish for example) and even people. These wastes may be either gaseous such as the fluorides, sulphuric oxides, nitrogen oxides and ammonia, or dilute water solutions which contain the above mentioned impurities and other compounds used or formed in the production process. In addition to waste waters and gaseous impurities solid wastes - gypsum, raw materials and the final products - are formed in the production process. The final products also yield wastes - dust in gases and solids in effluents. The fertilizer industry has done a great deal of work to minimize the harm done to the environment by wastes. Kemira Oy, a Finnish fertilizer company, has also worked on improving pollution control methods for the industry.

Since severe winters and shallowness make Finnish watercourses particularly vulnerable, Kemira Oy has concentrated on reducing the nutrient load on them, without neglecting the problems of purifying waste gases. The aim is to return the nutrients which enter waters to the process. This requires the adoption of various circulation systems and rational use of water. At the Siilinjärvi plants provisions are so advanced that even rainfall in the plant area which may pick up nutrients is included in the circulation system.

The subject of NO_x pollution problems was purposely omitted from this paper as it is being discussed by other papers at this meeting.

I. SULPHURIC ACID PRODUCTION

In producing sulphuric acid with the contact method, the type of wastes depend on the raw sulphur used. If elemental sulphur is used as a raw material, the only continuous effluents from sulphuric acid production are the SO_2, SO_3 and H_2SO_4 mist in stack gas.

A. Waste problems in the purification of roaster gases

When sulphuric acid is produced from SO_2 gases obtained in roasting sulphide ores, as is the case in Finland at present, the slurry of metal oxides formed in the purification of the roaster gases, the dilute sulphuric acid (approx. 30%) and also the gaseous impurities mentioned above cause environmental problems. The slurries mentioned above form because the dust and the halogens Cl and F from the SO_2 gas obtained in roasting must be removed to prevent poisoning of the catalyst.

The Soviets (1) have developed a so-called CO process based on special catalysts in which removing dust with an electric filter is enough to purify the roaster gases. The type of catalyst involved and where the impurities in the gas are conducted is not known for certain.

At certain plants the solid-containing solution obtained from scrubbing roaster gases is conducted along with the waste water into the watercourse. In some cases ships are even used to transport the acidic sludge out to sea.

Nowadays the prevention of the release of the sludges mentioned above is becoming increasingly widespread. In this case part of the solution from the gas scrubbing is conducted to the clarifiers for removal of the solid. The sludge obtained as an underflow is most often filtered again and returned to the roaster. The filtrate and part of the overflow from the clarifier is removed from the scrubbing circulation in order to prevent the chloride and fluoride contents from rising so high that they no longer remain in the scrubbing solution and poison the catalyst. The approximately 30% dilute sulphuric acid is used, e.g. in the production of superphosphate and also in the preparation of dilute montan salpeter solution at Kemira Oy's Kokkola plants. This solution is concentrated in vacuum evaporators and is used as a raw source of nitrogen in fertilizer production.

A special feature in the treatment of roaster gases is the recovery of mercury from the SO_2 (2) gas obtained in conjunction with zinc roasting. Recovery of this type is carried out at the Outokumpu Oy and Kemira Oy plants at Kokkola. The elemental mercury in the roaster gases in this process is converted into sulphate by scrubbing the gas with strong sulphuric acid in the sulphation tower. The mercury sulphate precipitate obtained is filtered and lime is added to it. It is then converted into an elemental mercury vapour by calcination. The calcination gases are conducted into the sulphation tower after condensation of the mercury. The gas coming out of the sulphation tower still contains a certain amount of mercuric sulphate in the sulphuric acid mist. This is removed from the gas in the purification section of the sulphuric acid plant and then enters the dilute sulphuric acid from which it is precipitated with sodium sulphide as a sulphide.

B. Removal of SO_2 from sulphuric acid stack gases

The following methods, which differ in principle, can be used for removing sulphur dioxide from the waste gases of the sulphuric acid process:

a) Improvement of SO_2 conversion to SO_3

b) Absorption with alkaline water solutions
c) Adsorption by ion exchange mass, active coal, etc.

$$SO_2 + 1/2\ O_2 \overset{\rightarrow}{\leftarrow} SO_3 + \Delta H$$

In order to reverse the above mentioned oxidation reaction as far as possible in the direction of the upper arrow, the following methods can be used:
a) increasing the amount and activity of the catalyst
b) reducing the SO_2 content of the reaction gas
c) reducing the temperature of the reaction gas
d) increasing the residence time
e) removing the reaction products.

Despite the fact that there is a reaction of gaseous compounds in which a reduction in volume occurs, there is no evidence that the pressure increase speeds up the reaction when the V_2O_5 catalyst is used. This is due to the fact that there is an SO_2 and O_2 diffusion through the SO_3 layer to the surface of the catalyst, which limits the reaction speed. Even if an increase in pressure raised the diffusion velocity, the SO_3 layer would also grow and the time taken by diffusion would remain unchanged (3).

A method based on the removal of the reaction products has now become the most popular of the above mentioned methods, designed to make conversion more effective. It is applied in the so-called double contact method. The double contact method in figure I differs from the conventional contact method in that the conversion of SO_2 to SO_3 occurs in two separate stages and before the gas enters the second stage the SO_3 (4) already formed is removed in its own absorption tower. Before this inter-absorption the gas is cooled and it must be heated before the next reaction stage.

The double contact method yields a 99.5% conversion while the normal method is only 98% effective. These figures correspond to 0.05% SO_2 contents in the stack gas with the double contact method and 0.15-0.12% with the conventional contact method.

In addition to the base used, the absorption methods also differ in another respect, depending on whether the SO_2 is recovered as a concentrated SO_2 gas or as the salt in question. The alkaline solutions used and the products obtained from them appear in table I.

Table I Absorption methods

Absorption solution	Recovered products	Remarks
Aqueous Na_2CO_3	Na_2SO_3, Na_2SO_4	
Aqueous MgO	SO_2	MgO is recirculated
Aqueous $KHSO_3$ - K_2SO_3	SO_2	SO_2 recovery via precipitated $K_2S_2O_5$
Aqueous $(CH_3NH_3)_2SO_3$	SO_2	SO_2 is stripped with steam from solution
Aqueous $Al_2(SO_4)_3$	SO_2	
Aqueous $Ca(OH)_2$-$CaSO_4$	$CaSO_4$ and $CaSO_3$	Normally products have no use.
Aqueous $(NH_4)_2SO_3$-NH_4HSO_3	SO_2 and NH_4NO_3	SO_2 is released with HNO_3 and heating
Two stage absorption first with 10% H_2SO_4 containing $MnSO_4$ and secondly with lime	SO_2 and $CaSO_4$ x 1/2 H_2O	

In purification methods based on adsorption active coal, coke and ion exchange masses are used as adsorption substances.

These are the Sulfacid process (Lurgi), the Hitachi process and the Reinluft process.

A process in which 50% sulphuric acid absorbs SO_2 and is then oxidized catalytically into sulphuric acid (1) has been developed in the Soviet Union.

Union Carbide has introduced the Pura Siv-S process for the removal of SO_2. This process is based on molecular sieves.

In the production of sulphuric acid the double contact method is the most suitable for the removal of SO_2 because none of the stages in it differ from the conventional contact process.

C. The removal of SO_3 and H_2SO_4 mist

Stack gases from sulphuric acid plants using the contact and double contact methods contain sulphuric acid mist formed from small drops of sulphuric acid. They are composed of water vapour and SO_3 and are formed in the vapour phase. The following mist elimination methods are used to remove the mist and the drops:

a) Dual Pad Mist Separators
b) Brink MIst Eliminators
c) Electrostatic Precipitation
d) Mist Removal with Venturi Scrubber.

The most effective of these are electric filters and Brink Mist Eliminators. The latter achieve 100% effectiveness with drops of over 3 μ and 99.8% with drops of less than 3 μ (6). Brink Mist Eliminators also require little space and this is another advantage in comparison with electric filters.

II. SUPERPHOSPHATE PRODUCTION

Superphosphate is obtained by treating raw phosphate with sulphuric acid. Wastes from superphosphate production develop in this stage, in which case 11-42% of the fluorides in the raw phosphate is released in the form of gaseous silicon tetrafluoride. The raw phosphates normally contain from 3.0 - 4.5% fluorides (8). The following are the reaction equations which release silicon tetrafluoride:

7) $CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\ HF$

8) $4HF + SiO_2 \longrightarrow SiF_4 + 2\ H_2O$

In addition to silicon tetrafluoride, gases from the superphosphate plant also contain a certain amount of hydrogen fluoride and phosphate dust. The gases are scrubbed with water in order to prevent the fluoride-containing gases from harming vegetation in the area around the plant or from posing a health hazard to the inhabitants. In this case the absorption of silicon tetrafluoride by water occurs in accordance with the following reaction equation:

9) $3\ SiF_4 + 2\ H_2O \longrightarrow 2\ H_2SiF_6 + SiO_2$

In fluoride absorption there is a transfer from air pollution problems to water pollution. Lime precipitation can be used for removing fluorides from the effluent, in which case impure calcium fluoride is obtained as a by-product. Circulation of the scrubbing solution solves the problem of effluents better than once-through gas scrubbing. Circulation permits the concentration of fluosilicic acid into a 15-25% solution. In order to prevent the fluoride content of the stack gas from increasing, despite the circulation, multi-stage gas scrubbing is necessary. This is because the growth in the concentration of the absorption solution also causes growth in the equilibrium concentration, i.e. the concentration gradient causing the mass transfer from gaseous phase to liquid phase decreases.

Another factor which must be taken into account is that silicic acid also develops in the reaction, as we saw from equation 9, and it may tend to plug up some scrubber types when it is in solid form. Thus the scrubber type must be chosen carefully. Silicic acid can be removed from the fluosilic acid by sedimentation or filtration. Centrifuges can also be used for removing silicic acid.

The fluosilic acid obtained can be refined in accordance with figure I into alkaline silicofluorides, aluminium fluoride and hydrogen fluoride through calcium fluoride and ammonium fluoride. The greatest difficulties in refining processes are caused by the elimination of silicon and phosphorus from the final products.

III. THE WET-PROCESS PHOSPHORIC ACID PRODUCTION

The following effluents develop when phosphoric acid is produced with the wet process.

a) phosphate dusts when handling raw materials
b) gases containing fluoride compounds when rock phosphate and sulphuric acid react together and when phosphoric acid is concentrated
c) acidic effluents in point b) when scrubbing the gases mentioned above and when washing the equipment; the effluents in question contain fluosilicic acid, phosphoric acid and gypsum
d) solid gypsum, which is separated from the phosphoric acid by filtration

The harmful effects of the phosphate dusts mentioned in point a) can be eliminated with effective dust collection equipment where dust is a problem, i.e. silos, unloading points, belt conveyors, etc. Dust is removed from dust-containing air with e.g.bag filters, and is then used in the process.

A. The purification of fluoride containing gases

The fluoride contained in the rock phosphate when phosphoric acid is produced with the wet method is distributed among the following:

- the phosphoric acid produced
- gypsum
- concentration and reaction gases

The fluoride distribution in the various fractions depends on:

1. the raw material used, e.g. sodium and potassium tend to precipitate silicofluorides
2. the process, more fluoride is released in high reaction temperatures
3. the strength of the acid produced, the more concentrated the acid, the more fluorides released.

At the Kemira Oy Siilinjärvi phosphoric acid plant 26% of the fluorine from the apatite used as a raw material goes into the gypsum, 34% is released in concentration and 40% remains in the 42% phosphoric acid.

In producing 30% phosphoric acid fluorides are released in the process stages mentioned in table 2.

Table 2. Gases containing fluorides in the phosphoric acid process

Process stage	Fluoride content	Fluoride removal from the gas
1. Reactor gases	200 - 700 mg/Nm^3	Individual gas scrubber
2. Vacuum cooler reaction slurry gases	300 - 1000 mg/Nm^3	Condenser scrubber, sometimes additional, individual scrubber
3. First filtration sector	100 - 200 mg/Nm^3	Individual gas scrubber
4. Filter vacuum system		Condenser scrubber
5. Filter tanks and storage tanks	50 - 100 mg/Nm^3 from the first tank	Individual gas scrubber

Table 2 also indicates the stage in which the fluorides are most often removed. It must be remembered that solid silicic acid forms in scrubbing gases containing fluorides and this may plug up the scrubber.

Since the fluoride content in the phosphoric acid process itself is rather low, a max. of 1 g/Nm^3, fluorides are not normally recovered from these gases. They are merely scrubbed in equipment operating on the once-through principle with pure water or circulation water taken from the gypsum basin. There may sometimes be a separate circulation system for these waters.

In concentrating phosphoric acid, the fluoride amount released and the fluoride content are greater than in the process itself, the fluorides are normally recovered in the form of 15-25% fluosilicic acid. When using vacuum evaporation, fluoride recovery takes place in the scrubber located between the flash chamber and the condenser. In order to prevent the drops of phosphoric acid from entering the silicofluoric acid there is usually an effective drop eliminator before the scrubber. Spray towers are most generally used as scrubbers.

B. The treatment of acidic effluent

In order to prevent the detrimental effects of the acidic effluents produced in the phosphoric acid process (this includes harm to fish caused by acidity or fluorides, raising the fluoride content of the watercourse to the extent that it is unsuitable for other use and eutrofication caused by phosphorus) one can either treat the effluent before it is released into the watercourse or reuse the water in the process. Lime can be used as the chemical in purification, in which case the fluorides and phosphorus are precipitated. However, it is generally more economical to reuse the water in the process. The concentrations in the water are kept from rising by taking the water for gypsum washing from the circulation or by using e.g. lime treatment.

C. Gypsum disposal

Many phosphoric acid plants still dispose of their by-product gypsum by conducting it to the watercourse in the form of a sludge in the cooling water. Dry storage of gypsum on land is more effective for pollution control. Gypsum is conveyed to the storage area in the following ways.

- pumped as a water sludge, the sludge water returned to the plant
- dry transport on belt conveyors
- dry transport by truck.

Storage may cause problems for the land area due both to effluent difficulties caused by rainfall and to the detrimental effect on the landscape.

Effluent problems can be solved by the method mentioned in section 5.2.

For pollution control it is best to reprocess the gypsum. Gypsum can be reprocessed in the following ways:

a) gypsum sheet or plaster for the construction industry can be produced
b) use as an additive in the production of cement
c) ammonium sulphate can be prepared, in which case there will also be a calcium carbonate by-product.
d) sulphuric acid and cement can be produced.

Alternatives a) and b) require additional purification of the gypsum before use. Alternative c) requires that a use be found for ammonium sulphate in e.g. the fertilizer industry. The preparation of sulphuric acid from gypsum depends on the availability of other cheap sulphur sources. If there are no such sources, then it may be an economical way to dispose of the gypsum.

IV. COMPLEX FERTILIZER PRODUCTION

As raw materials in the form of solids, sludges, liquids and gases are used in the production of compound fertilizers, there are also wastes in all these forms, making pollution control complex. Unless efforts are made to reduce the wastes released into the environment, substantial losses in production will result in some cases. It is natural that economic factors also call for reductions in the wastes released into the environment.

Solid wastes - dust from raw materials and the final products - are produced in unloading, transferring and storage of the raw materials and in drying, cooling, crushing, screening and transport of the products, both at the plant itself and in the process of storing and sacking.

The oxides of nitrogen, ammonia, silicon tetrafluoride, and hydrogen fluoride and in some special cases hydrochloric acid are the gaseous impurities that appear in the compound fertilizer process. Gaseous impurities are released from the process to some extent in granulation and drying in addition to the reaction stage (neutralization and also dissolution in the nitrophosphate process).

Waste water from the fertilizer process contains undissolved and dissolved fertilizers, ammonia, fluorides, i.e. nutrient and fluorides. These nutrient and fluoride-bearing waters develop in scrubbing the reaction and drying gases, washing the equipment, and in conjunction with sealing leaks in the pumps and other leaks.

A. Purification methods used in the fertilizer production

Efficient cyclone batteries, bag filters or wet scrubbers are used for removing dust from the bases evolved in the fertilizer process. The bag filter is the most effective of these, although there are drawbacks which prevent a solution to all the problems of dust elimination in fertilizer production. The following are the drawbacks:

- the heat resistance of the filter cloths is rather restricted since chemical resistance is also required
- it is not suitable for hygroscopic dusts
- going below the dew point plugs up filter cloths
- rather high maintenance costs
- takes up a lot of space

Due to the detrimental effects caused by moistening, bag filters cannot be used for granulation gases nor for dust removal from dissolution and neutralization gases. Simultaneous heat and chemical strain limit the use of bag filters in removing dust from drying gases. Filter cloth materials will probably be available in the next few years which will resolve the problems in question. Bag filters are used successfully in the fertilizer process for eliminating dust from cooling gases, from general dust collection systems' gases (gases ventilated to prevent dusting in sieves, crushers, conveyors etc.) and from the exit gases from raw material silos. The bag filter is also economical at the points mentioned since it does not require a wet scrubber. This is because there are no gaseous impurities in the gases in question. In contrast, cyclone batteries most often require a wet scrubber because their efficiency for so-called fine dust, the type produced at fertilizer plants, is only from 70-80%(9).

Since the gases produced in drying fertilizers contain gaseous impurities such as ammonia, fluoride compounds and sometimes the oxides of nitrogen in addition to dust, the gases usually require both wet scrubbing and dust elimination in cyclone batteries. The scrubbing solution used for both drying gases and granulation gases must be made acidic in order to recover the ammonia. Either sulphuric or phosphoric acid can be used, depending on the process. if phosphoric acid is used, the molar ratio should be 1.3, for there is a danger of crystallization of the ammonium phosphate when the molar ratio is in a range from 0.8 to 1.3. In fact, similar crystallization has appeared when sulphuric acid was used. An acidic scrubbing solution must also be used in order to avoid losses of ammonia in scrubbing the gases in the neutralization reactor.

As water evaporates in the scrubber, nutrient containing leakage and washing water produced at the plant can frequently be fed into the scrubbing circulation to compensate for the evaporation. Of course a collection system for the nutrient containing leakage and washing water must be built. Gases released from the dissolving reactor in the nitrophosphate process contain fluorides and oxides of nitrogen. There must be a separate gas scrubber for them. In order to make recovery of the impurities in question - the oxides of nitrogen in particular - more effective, an alkaline scrubbing solution can be used in which case ammonia, lime, sodium carbonate and magnesium hydroxide can be used as a base. If circulation solutions are used in the purification of waste gases from the fertilizer process, in the manner mentioned above, the gas scrubbers must be of a type that does not get plugged up and special attention must be placed on drop elimination.

In order to prevent waste waters from forming, the resulting solutions must be fed, depending on the process, to either the reactors or granulation. Of course this requirement must be taken into account in choosing the raw materials and in dimensioning the drying equipment if the scrubbing solutions are to be used. For example, this means that 50% P_2O_5 phosphoric acid is necessary, while 40% P_2O_5 is sufficient when the gas scrubbing solutions are not used. Therefore it is frequently impossible to use the gas-scrubbing solution circulation mentioned above at existing plants without changing either the raw materials and the reaction conditions or the capacity.

V . ENVIRONMENTAL PROTECTION AT KEMIRA OY'S SIILINJÄRVI PLANTS

The Siilinjärvi plants are in central Finland on the upper reaches of a very clean watercourse. There is enough clean water for the plants' use, but very limited possibilities for releasing waste water. Evidence of the water's cleanness is indicated by a hardness of 0.5-1.5 DH^O, a phosphorus content of 0.02 mg/l and a nitrogen content of less than 0.1 mg/l. The lake from which the Siilinjärvi plants take their water supply and into which they conduct their cooling water must be carefully protected from excessive phosphorus loadings, for phosphorus is a factor regulating the growth of algae in the lake. It has been demonstrated experimentally that if the phosphorus content grew from the present concentration of 0.02 mg/l to 0.04 mg/l, substantial algae production would begin in the lake during the summer.

Even more generally, phosphorus acts as a limiting factor on eutrophication in Finnish lakes. The same applies in our maritime bays, for they resemble inland lakes and water exchange is limited. Algae production is substantial in spring and is especially dangerous because watercourses are covered with ice in winter. The algae mass sinks to the bottom and breaks up using up the oxygen in the water in the process. This naturally kills the fish and other organisms in the water or drives them away first. The result is the pollution of the lake to the extent that both recreational and industrial use are impossible.

Long, cold winters also make Finnish vegetation susceptible to airborne impurities. Our conifers in particular suffer from pollution during the winter.

The Siilinjärvi plants are rather new. The first stage was completed in 1969 and comprises a roasting plant and sulphuric acid plant (230,000 tons a year), phosphoric acid plant (75,000 tons a year of P_2O_5), a monammonium phosphate plant (150,000 tons a year), and a power plant. The second stage was largely completed in 1972 and includes a nitric acid plant (85,000 tons a year), a complex fertilizer plant (200,000 tons a year), and fertilizer stores and a sacking plant. The extension of the phosphoric acid plant, which is part of the second stage, was completed at the end of 1973, and phosphoric acid capacity is now 120,000 tons a year.

The starting premise for environmental protection at the Siilinjärvi plants was that all stack gases should be scrubbed and that no nutrient-containing water should be released into the environment. This would eliminate the detrimental effects mentioned above.

Water supply and waste water systems appear as a scheme in figure III.

The plant takes the water it needs from a nearby lake. The quantity of water is approximately 3800 cu.m/h and it is mainly used for cooling at the power plant, the sulphuric acid plant and the nitric acid plant. Clean, only heated cooling water from these plants is returned to the watercourse.

Nutrient-containing waters formed in the processes have their own circulation systems. Most of the nutrient-containing rain water is conducted to these circulation systems. More dilute rain water in the plant area is conducted to the watercourse after removal of the phosphate with lime. The phosphorus content after purification is 0.1 mg p/l and the water quantity in 1973 was approximately 130 cu.m/h on average. This figure also included all the municipal effluents formed at the plants. Biological purification of these effluents takes place before the phosphate removal. The total quantities of nutrients entering the watercourse along with the cooling waters and the treated municipal effluent and rainfall were 3.4 kg P/day and 31.1 kg N/day in 1973, computed as an average.

A. The sulphuric acid and roaster plant

The sulphuric acid plant uses SO_2 gas obtained from roasting the pyrrhotite and the plant operates with a conventional contact process, achieving 98% conversion. Stack gases are conducted through a 90 metre chimney. The sulphuric acid and solids-containing scrubbing solution, formed in the purification of the roaster gases, is used for moistening the roasted product before it is conveyed to the waste area. Sulphuric acid-containing leakage which occasionally occurs at the sulphuric acid plant, is conducted into the circulation water pond of the phosphoric acid plant.

Clean, only heated cooling water is conducted from the sulphuric acid plant to the watercourse. The quantity is approximately 2,400 cu.m/h. 80% of this quantity is already used at one time as cooling water for the condenser of turbine at the power plant.

B. The nitric acid plant

The nitric acid plant operates at a pressure of 3.9 aty and the NO_x content after the absorption tower is 0.06% during the warmest period in summer and 0.03% in winter, in which case the cooling water is cold. Overdimensioning of the absorption tower permitted us to achieve these figures. Nitric acid leakage water is also conducted from here to the circulation water pond of the phosphoric acid plant.

C. Phosphoric acid and monoammonium phosphate plants

The phosphoric acid plant operates with the normal dihydrate method. The 29% acid obtained from the filter is concentrated with the vacuum evaporators to either 42% or 50%, according to needs. Vacuum coolers are also used to cool the reaction slurry.

Fluoride-containing gases released in reactors, and filters and storage tanks are scrubbed with circulation water in venturi and floating bed scrubbers operating in series. This floating bed scrubber, the second stage in scrubbing the reaction gases mentioned above, and the gas scrubber for the filter, have the same circulation tank. This last mentioned scrubber is also a floating bed type with three ball layers. Additional water, some 30 cu.m/h, enters the gas scrubbers' circulation tank from the phosphoric acid plant's circulation system (figure IV). Circulation water of the phosphoric acid plant is used in the condenser-scrubbers of the vacuum coolers for the reaction slurry and in the condenser-scrubbers for the filters. Heated circulation water obtained from the condenser-scrubbers is used for scrubbing the filter cloths and further for washing the cake. Water removal of this type prevents the concentrations of the circulation water from increasing. Circulation water of the phosphoric acid plant is also used in the condensers at the phosphoric acid concentration plant. Water is pumped from the phosphoric acid and concentration plants through the cooling tower to the 2-hectare circulation pond. Spring flood waters from the 25 hectare gypsum area must be stored in the pond, and this determined the regulating volume of the pond. Rain water from the gypsum road and the gypsum area mentioned above, leakage water from the sulphuric acid and nitric acid plant's laboratory water and sealing water from the phosphoric acid plant's pumps make up the water used in washing the gypsum and that evaporated in the cooling tower.

Fluorides released when the phosphoric acid is concentrated is recovered as a 25% solution of fluosilicic acid. The fluosilicic acid recovered is shipped by rail to the Kemira Oy Uusikaupunki plants where it is processed into alkaline silicofluorides in conjunction with an installation operating at the company's oldest phosphoric acid plant. The fluorides are recovered in the spray tower. Efficient impingement type drop eliminators are located before and after the tower. The unit before the spray tower is intended to eliminate the phosphoric acid drops from the concentration gases. The eliminator after the spray tower is designed to reduce the fluosilicic acid drops entering the condenser. Thus the last mentioned is designed to improve the recovery of fluorides and at the same time reduce the amount of fluorides entering the circulation water in the condenser.

Only the cooling waters from the instrument air compressors and the sealing waters from the vacuum pumps are conducted from the phosphoric acid plant and the concentration plant into the watercourse. Approximately 7 kg F/day entered the watercourse in 1973, computed as an average for the entire year.

The only source of impurities at the monoammonium phosphate plant is the neutralization reactor. The ammonia released from it is recovered in a Doyle type gas scrubber by washing the gas with the phosphoric acid to be used in the process. Since phosphoric acid with a P_2O_5 content of 42% is used to recover NH_3 from gas at a temperature of 80°C, fluorides are released from the acid into the gas. In order to pick up the fluorides, the gases are washed with circulation water from the phosphoric acid plant in two venturi scrubbers operating in series. No other effluents are formed in the production of monoammonium phosphate.

Gypsum is transported from the filter at the plant first by a belt conveyor and then about 800 m by truck. Since annual rainfall in the Siilinjärvi region of Finland is about 600 mm and evaporation is about 300 mm, phosphorus and fluorides containing rain water coming from the gypsum area are either purified before being conducted into the watercourse or otherwise prevented from entering it, so that the watercourse is not polluted. At the Siilinjärvi phosphoric acid plant the rain water problem is resolved by collecting the rainfall in the phosphoric acid plant's circulation water pond. A treatment plant based on lime precipitation was built to handle flash floods. If necessary, the regulation capacity can be increased fivefold.

Waste gases from the phosphoric acid plant and the monoammonium phosphate plant are conducted to the joint chimney. According to waste gas measurements made in April 1974, the following amounts of impurities were released into the environment along with waste gases from the plants.

8.8 kg/h NH_3
2.6 kg/h F
3.0 kg/h dust

D. The complex fertilizer plant

The complex fertilizer plant was designed and built by Kemira Oy. The process is the nitrophosphate type, which uses phosphoric acid and, if necessary, sulphuric acid to stabilize the calcium and as an aid in obtaining water soluble phosphorus. It has four reactors in series. In the first two reactors phosphate rock is dissolved in nitric acid. The next two reactors are ammoniation units. Phosphoric acid and sulphuric acid are fed into these reactors according to the grade being manufactured. The solid raw materials, such as potassium chloride, are fed into the last neutralization reactor. The neutralization reactions are heavily exothermic and the heat developed is used for water evaporation. The reactors are water-cooled, the idea being to lower the temperature and at the same time reduce the amount of effluents discharged with the gas.

From the fourth reactor the NPK slurry flows along the overflow into the pumping tank, from which it is pumped into two adjacent spherodizers in which the granulation and drying take place. This stage is followed by screening and crushing. The screened undersize, crushed oversize and some of the commercial size are returned to the spherodizer and only the screened, desired amount of the final product passes via cooling and coating into the warehouse.

The fertilizer factory's main effluents are:
- gases from the reactors and spherodizers, comprising ammonia, the oxides of nitrogen and fluorine
- dusts from the spherodizers, from the cooling process and from handling of the solid product in general
- nutrient-containing water, seepage water, machinery wash water, pump sealing water, etc.

The exit gases from the spherodizers contain fertilizer dust, and ammonia and the oxides of nitrogen released during drying. The gas is led first into high efficiency cyclone batteries, in which the dust is separated dry and returned to the reactors along conveyor spirals.

The dust in the exit gases from the cooling drum are separated with a bag filter. A bag filter is extremely suitable for the separation of very fine, dry dust and gives a splendid separation effect - about 99.8%. Using a bag filter gives a very good purity result in a dry way and avoids using water, which always involves problems with discharge of the water.

The general dust collection systems collect dust from e.g. the following places:

- the belt conveyor and bucket elevator discharge points
- the screens
- the crushers
- the coating drum
- the scales

These dusts are collected in a bag filter, separated and returned to the reactors.

All the dusts are returned to the reactors, in which they are mixed into the slurry and fed back into the granulation process.

Scrubbing systems

Waste gas scrubbing must be used when both gaseous components and dust have to be removed or when extremely good dust separation is not possible using a dry method due to the properties of the waste gas.

The reactors' exit gases contain ammonia, the oxides of nitrogen and fluorides. The gases are scrubbed in two lines, each of which has two scrubbing stages. The chloride limit has been used as the dividing principle: the gases entering one scrubber come from the dissolving reactors and the first neutralization reactor and those entering the second line from the second neutralization reactor and the pumping tanks, which contain chloride-bearing NPK slurry. The first reactors evolve more fluorides and oxides of nitrogen containing gases, and these are acidic like the slurry in the reactors. In this kind of environment the chlorides would be very corrosive so the gases must be handled separately. The recovery of fluorides and the oxides of nitrogen is still very difficult, so the gas scrubbing is separate, to make it possible to use as much clean scrubbing liquid as possible and to produce the best possible scrubbing result.

The scrubbers are called "floating bed scrubbers". They are packed scrubbers which are filled with light balls which move in a stream of air and are made of plastic. Each scrubber has three layers of balls.

Closed water circulation system

Each scrubbing stage has its own water circulation (fig. V). Thus make-up water is led into the second, i.e. last, stage of the gas scrubber of the first reactors. It then flows back to circulate in the first stage. From here the water is pumped into the first reactors.

The make-up water comes into the gas scrubber of the chloride-bearing reactors from the spherodizers' gas scrubbers. When the scrubbing liquid has gone through both stages of the unit, flowing countercurrent to the gas, it is pumped into the second neutralization reactor. The amount of water pumped from the gas scrubbers into the reactors is 4 - 7 cu.m/h depending on the reaction heat of the grade of fertilizer being made. The higher the reaction temperature, the more scrubbing water can be pumped into the reactors, the lower the nutrient and solid matter content of the scrubbing liquid, and the better the scrubbing effect.

The exit gases from the spherodizer are led each into its own gas scrubber after the cyclones. These scrubbers are also of the floating bed type and each has two layers of balls. The scrubbers have a joint circulation tank, and clean or rain water is led into this as make-up water. The scrubbing liquid is made acidic with phosphoric or sulphuric acid so that the pH is about 5. This makes the ammonia stay in the scrubbing liquid. Since crystallization difficulties have arisen in the recovery of ammonia with sulphuric acid, it is now considered better to use phosphoric acid. Part of the scrubbing liquid is evaporated adiabatically and part is pumped into the second reactor gas scrubber in the way mentioned earlier.

All the nutrient-containing water produced at the fertilizer factory, such as seepage water, pump sealing water, machinery wash water and laboratory water, is collected in a floor sump. The cooling waters and condensate are led there automatically when their conductivity gives the alarm, indicating that salts have got into the cooling water. From the floor sump the water is pumped into the water circulation system of the spherodizers' gas scrubbers. If a particularly large amount of water is produced in some catastrophy situation, it overflows into the fertilizer factory rain water basin.

This rain water basin collects all the rain water in the fertilizer store and sacking plant areas and from the yards around the fertilizer factory proper, i.e. all the water which may contain nutrients. The surface area draining into the basin is about 3.5 hectares, and its regulation capacity about 4,000 cu.m. From the basin the water is pumped into the gas scrubbing process as make-up water.

This closed gas scrubbing water circulation system and the rain water basin described above have the advantage that nutrient-bearing water does not leave he factory at all. All the water is fed to the reactors via the scrubbers and the only water leaving the system is in the form of steam, with the exit gases.

Due to the environmental protection measures outlined above, the fertilizer factory effluent is limited to that discharged with the gases. This consists of the following at this factory, which produces 750 tons a day.

- total F 1 kg/h
- total N 12 kg/h
- dust 15 kg/h

E. The costs of environmental protection

Environmental protection carried out at the Siilinjärvi plants will cost a total of 11.33 million marks. The breakdown is the following:

- the first stage of the circulation water system for the phosphoric acid plant - 1969	3.5 million marks
- the rain water collection system at the fertilizer plant - 1972	0.6 million marks
- collection of rain water from the factory area and treatment - 1972	0.6 million marks
- treatment of waste gases and circulation of water at the fertilizer plant - 1972	4.22 million marks
- changes in the circulation water system of the phosphoric acid plant in conjunction with expansion - 1973	1.44 million marks
- improvement of gas scrubbing at the phosphoric acid plant - 1973	0.97 million marks

The costs listed above do not include those incurred in recovery of fluosilicic acid at the phosphoric acid concentration plant or the additional costs incurred in overdimensioning the absorption towers of the nitric acid plant.

In 1972 environmental protection costs at the fertilizer plant completed that year accounted for 19% of the total investments for the fertilizer plant and the operating costs incurred in environmental protection at the beginning of 1973 accounted for 8.8 Finnish marks/t of the fertilizer produced. Here the operating costs include the additional expenditure incurred in the concentration of phosphoric acid from 35% P_2O_5 to 50%.

It can be shown that environmental protection costs as a proportion of total investments at the new installation have more than doubled in the past ten years. At the same time environmental protection costs in the price of a fertilizer ton have grown about tenfold. Thus not only the investments made in environmental protection itself, but the operating costs incurred in the steps taken have also risen greatly.

VI. CONCLUSIONS

From the point of view of protection of the environment, however, it is not enough for plants to be equipped with first-class modern environmental protection equipment. It is particularly important for the equipment to be kept in good working condition all the time and for it to be checked, as top equipment calls for top control and maintenance. It is this work of control and maintenance that results in considerable operating costs.

In recent years new pollution control methods and equipment have been developed for the use of the phosphate fertilizer industry and the captive acid industry. Nowadays there are often several different alternatives for a single environmental protection problem. The solution must be made on the basis of local conditions in each case and no solutions are valid everywhere.

Advancing technology has produced new equipment and methods but at the same time costs have risen substantially. Rising costs of course reduce the profitability of production and in some cases may even mean production has to close down. However, our environment is so important to us that we can't just sit and lament if production of some product has to stop if this means that our environment continues to be worth living in. Technology will go on advancing and offering new answers to the pollution problem and the protector of the future environment may well react to our present methods rather as we react to the old alchemists not only in the scientific but also - and specifically - in the technical sense.

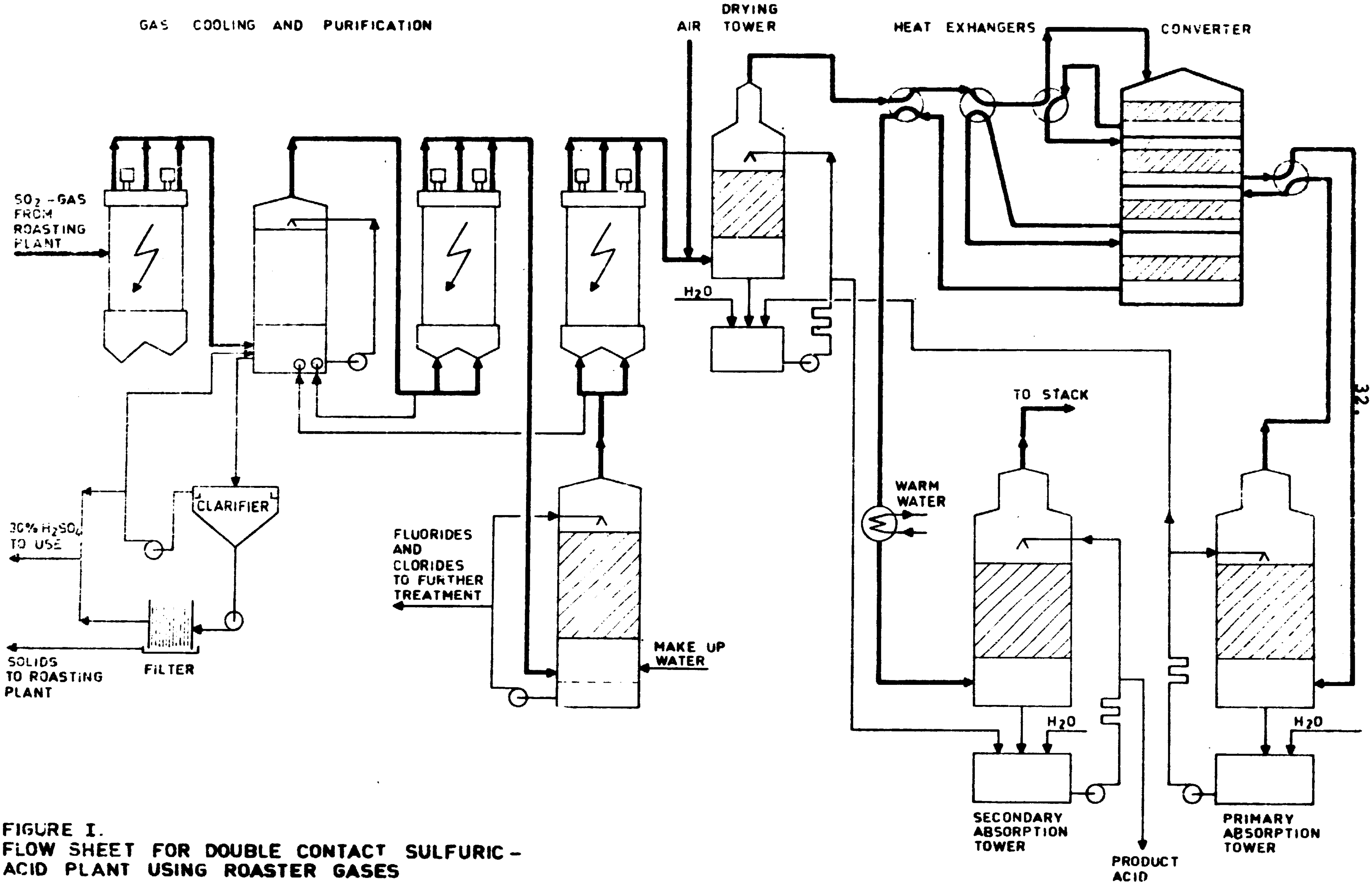

FIGURE I.
FLOW SHEET FOR DOUBLE CONTACT SULFURIC-ACID PLANT USING ROASTER GASES

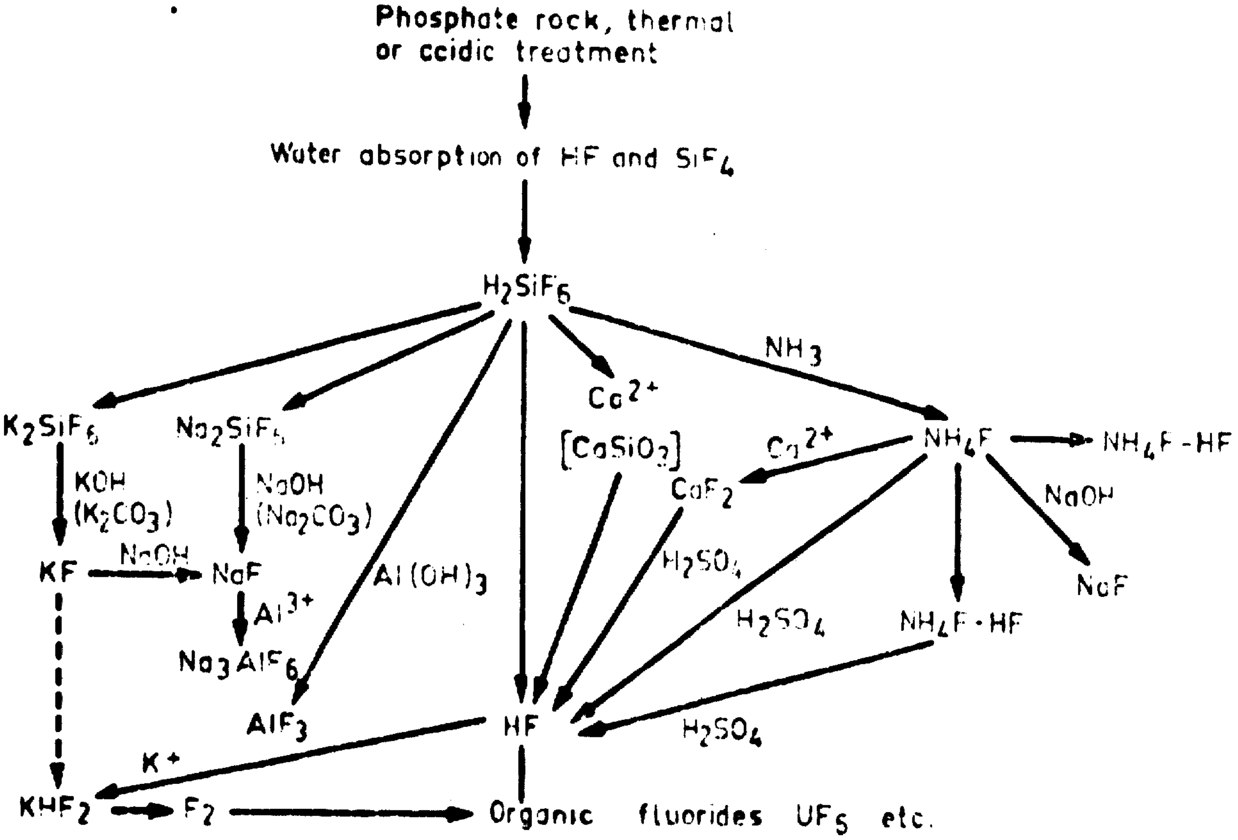

FIGURE II. FLUORINE COMPOUNDS AS BY-PRODUCTS OF THE PHOSPHATE FERTILIZER INDUSTRY

FIG III WATER AND WASTEWATER SCHEME
SIILINJARVI WORKS

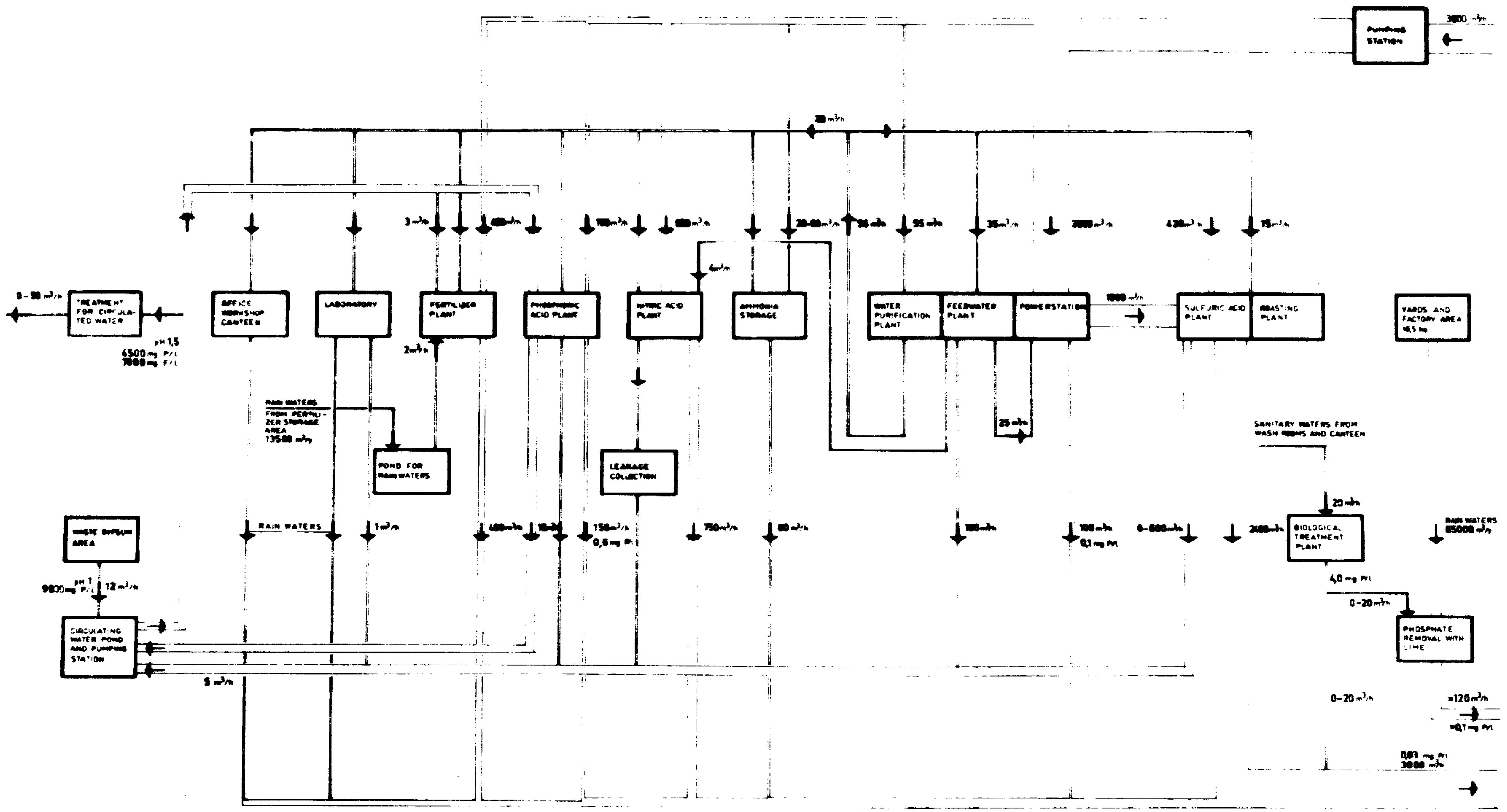

FIG. IV WATER SCHEME FOR PHOSPHORIC ACID PLANT

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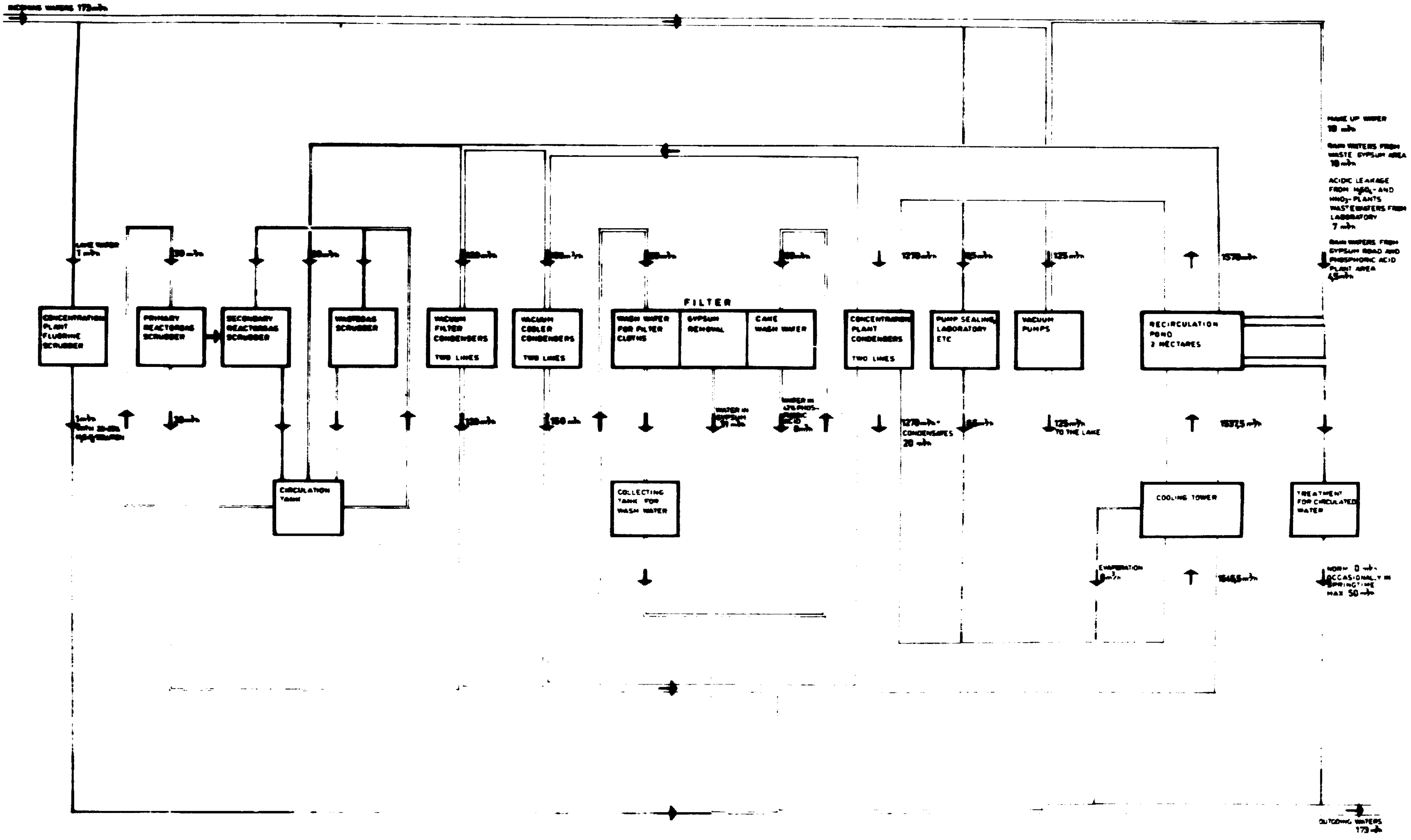
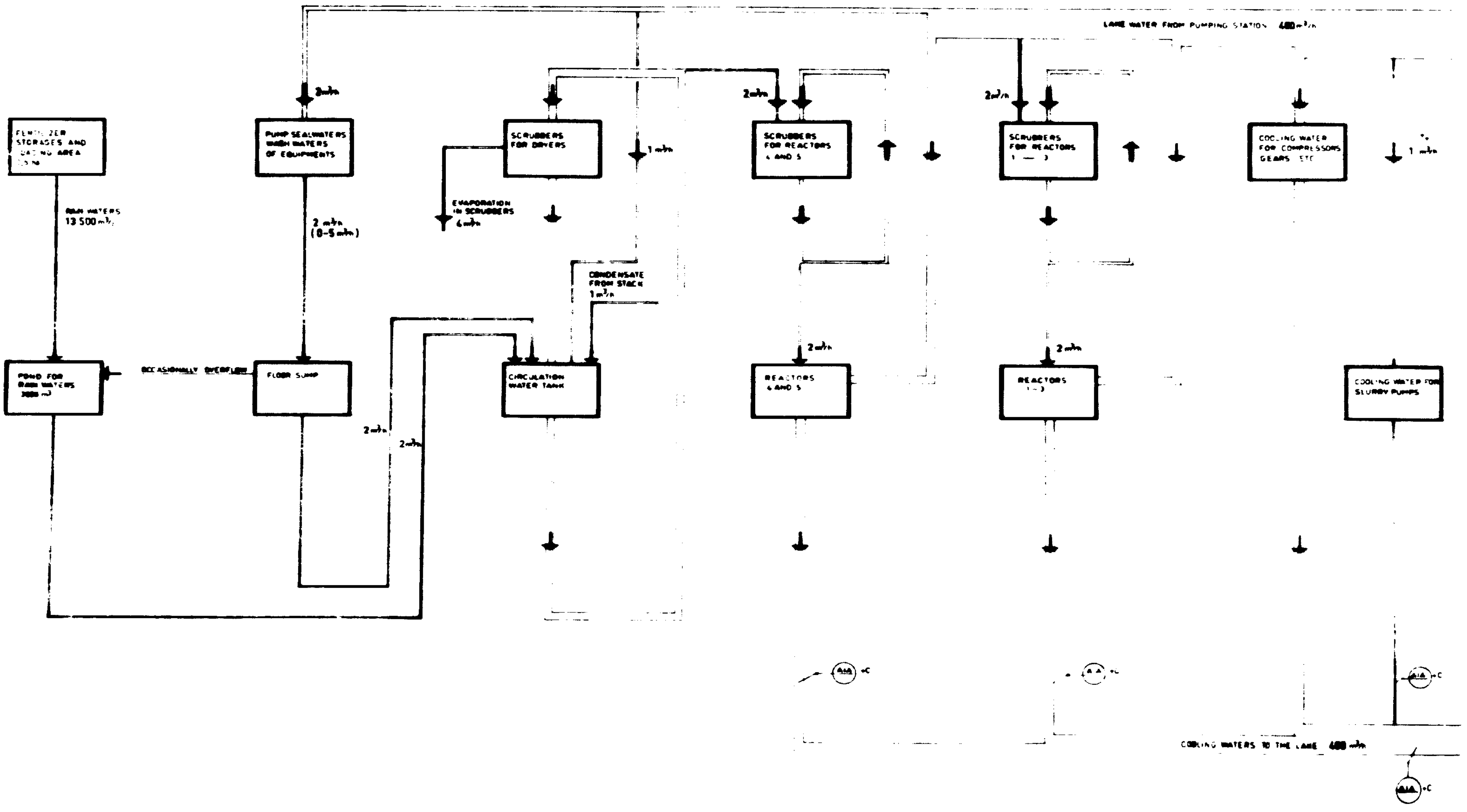


BALANCE CALCULATION FOR PRODUCTION OF 90000 t P_2O_5/YEAR

FIG V WATER SCHEME FOR FERTILIZER PLANT

SIILINJARVI WORKS



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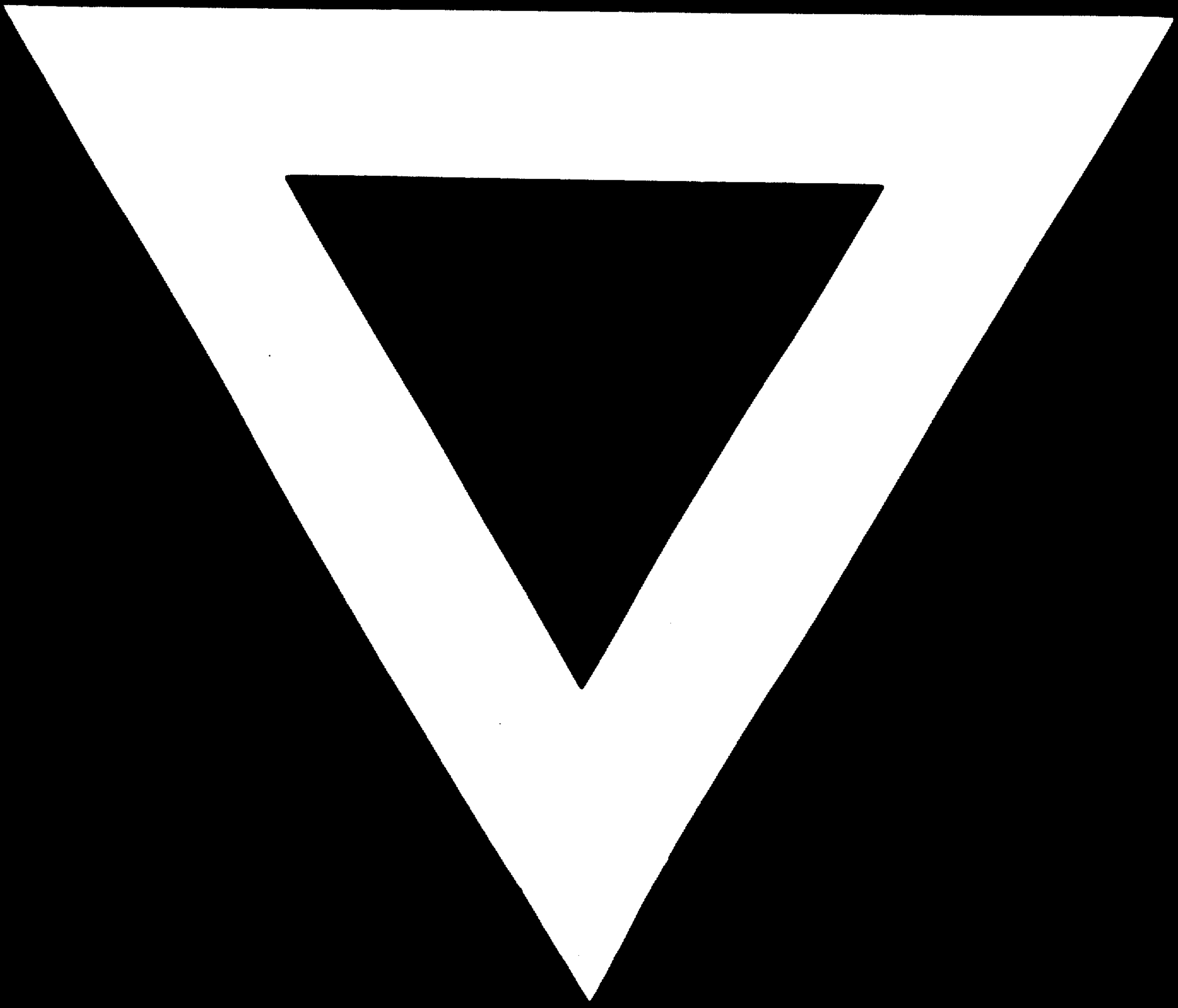

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