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SPHERODIZER GRANULATION OF NPK BY NITRIC ATTACK: PROCESS AND ENVIRONMENTAL ASPECTS

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1] INTRODUCTION

Several types of NP and NPK fertilizers are produced by the Enimont complex fertilizers plant in Ravenna, the initiating factor being nitric acid attack on phosphates, utilizing spherodizer granulation technology. This technology was opted for during the plant revamping, performed in 1975, in order to achieve increased production capacity, and a wide range N/P205 ratio [from 2, 5/1 to 1/3], together with improved granule quality. **Current production capacity is more than 400,000 tonnes/year.**

It is a well known fact that the process involving nitric attack on phosphates and granulation, forms gases and powders which are hard to handle in environmental terms, unless they are suitably treated. Up until 1986, the reaction gases [acid and ammoniacal], were treated in a water absorption type column, whereas the powder from the spherodizer fumes was dry separated through cyclone trains.

In conformity with the local authority laws in force, a chemical effluent scrubbing unit was later constructed, having the capacity to treat all emissions, up to the point of being within the limits set by the said authority. The key aspect of the project lay in the level of water consumption, and the possibility of neutralizing the recovery solutions. Precise calculations were done in order to assess the water consumption for all possible combinations of fertilizers produced by the plant at issue. The resulting data laid the foundations for the project, which made complete recovery of the solutions from scrubbing possible.

2] PROCESS DESCRIPTION

The production process consists of combining several raw materials [**nitric acid, ammonia, phosphates, monoammonium phosphate, ammonium sulphate, ammonium nitrate, potassium chloride, potassium sulphate**], by means of chemical reactions and straightforward physical mixing, to produce a single end product, comprising the three basic fertilizing elements: **nitrogen [N], phosphorous [P] and potassium [K]**, in different concentrations. The addition of small quantities of magnesium, boron and certain metallic ions is provided for some products.

The larger scale production is for the following:

12-12-12	16-35-0	11-22-16
15-15-15	25-10-0	12-06-18+2MgO
20-10-10	23-23-0	8-24-24
20-10-10 S		18-18-05

The plant comprises three sections in series: **reaction, granulation and effluent treatment**, and daily production capacity is in the range of 1000/1500 tonnes.

2.1] <u>REACTION SECTION</u>

The basic raw material consists of natural phosphates BPL/72-79 [33-36% P2O5], which are attacked by 60% nitric acid to produce monocalcium phosphate, calcium nitrate and phosphoric acid. Considering only the main elements [Ca, P] the involved reactions are as follows:

$$P_2O_5 \times 4\ CaO + 6.8\ HNO_3 \rightarrow 0.6\ Ca[H_2PO_4]_2 + 3.4\ Ca[NO_3]_2 + 0.8\ H_3PO_4$$

In the aim of eliminating calcium nitrate, which reduces the quality of the salt, monoammonium phosphate [$NH_4H_2PO_4$] is subsequently added, reacting as follows:

$$0.6\ Ca[H_2PO_4]_2 + 3.4\ Ca[NO_3]_2 + 0.8\ H_3PO_4 + 2\ NH_4H_2PO_4 \rightarrow 4\ CaHPO_4 + 2\ NH_4NO_3 + 4.8\ HNO_3$$

The high degree of acidity produced is then neutralised by reaction with gaseous ammonia:

$$4\ CaHPO_4 + 2\ NH_4NO_3 + 4.8\ NH_3 \rightarrow 4\ CaHPO_4 + 6.8\ NH_4NO_3$$

The neutralisation heat, equivalent to ≃500 Kcal/kg NH_3 is utilised for the partial evaporation of the water present in the attacking slurry.

The potassium, where necessary, is supplied by adding either potassium chloride, or potassium sulphate. The final nitrogen concentration is achieved by metering suitable quantities of ammonium sulphate and ammonium nitrate. Should magnesium be required, it is added as an acid solution, or as ground dolomite.

The above-mentioned reactions take place in a train of 19 reactors. Phosphate attack by nitric acid occurs in the first three reactors. Monoammonium phosphate is added in reactors 4, 5 and 6. Slurry neutralisation by means of ammonia addition occurs in reactors 7 and 8. Raw materials which are not involved in the reaction [**potassium chloride, boron, metallic ions**], are metered into the remaining reactors. If an inert substance is required to achieve the desired concentration, gypsum is added.

Every reactor runs under slight vacuum, as they are connected to the suction of a fan. All the reactors are made of stainless steel, AISI 316 L, apart from the first three, which are made of Uranus B6, since they run at pH <2. They are "U" shaped, volume $2m^3$, fitted with two stirrers, one with suction blades, drawing the slurry to reactor exit, and the other with pressure blades to mix and transfer the reaction products.

The ammoniation reactors [7^{th} and 8^{th}], are an exception. The volume of each one is 25 m^3, and the internal mixing device is based on a proprietary design.

During the ammoniation phase, the slurries reach very high viscosities, creating stirring problems in the "U" shaped reactors.

The reactors which are actually utilised, feature both a geometric design and a stirring system suitable for transferring even the very viscous slurries. Ammonia is blown in through eight jets, positioned on the reactor bottom, along the whole perimeter, and the quantity is automatically adjusted by a pH-meter.

The gases, produced during reaction, are scrubbed in the special treatment section which is described in paragraph 3.1.

2.1.1 TYPICAL MIXES

	15-15-15 %	25-10 %	20-10-10 S %	12-6-18+ 2 MgO %
Phosphate	11	14.5	11	13.9
Map 10-50	17.6	10.4	4	2.6
HNO3	12.8	15.5	11.4	14.1
NH3	4.0	3.4	3.9	1.6
NH4NO3	16.6	46.4	39.7	14.8
[NH4]2 SO4	8.6	9.8	2.0	1.1
KCl	26.0	-	-	-
H3PO4	4.0	-	6.5	-
K2SO4	-	-	21.2	38.0
Dolomite sol. [N:17.5-MgO:12.5]				12.9

2.2] SPHERODIZER GRANULATION UNIT

Further to reaction, the fertiliser slurry [u=500 cP H2O=12 - 22%, pH = 3.5 - 6.3, T= 120°C], is pumped to the granulation section, which comprises two parallel lines with spherodizers [L=12m, diameter=4.25m rpm= 4.23].

Two of the main fertiliser production phases are performed by the spherodizer: granulation in the first section, and drying in the second section.

Granule growth is achieved by nozzles, which spray the reaction slurry with a fine cloud of droplets, in a rotating drum, on a bed of basic fertiliser nuclei at least 40 mesh in diameter, and moisture content below the caking point.

Hot air, produced by a methane burner, flows through the horizontal axis rotating drum in the same direction as the product flow. The front part of the cylinder is fitted with vanes along the lateral surface, which lift the product mass, letting it fall once again during rotation, thus forming a falling layer which fills the transverse section. The slurry is then sprayed onto the falling layer of forming grains [basic nuclei].

When the droplets come into contact with the surface of the granule, the surface moisture exceeds the caking point, and then drops rapidly below the caking point since the air present is at a sufficiently high temperature, but not enough to damage granule roundness, which is aided by drum rotation.

As the granules travel around the cylinder, they are covered by films until the final dimension is reached.

During the continuous production process, the spherodizer is fed with fine recycle granules from the vibrating screen section, which are utilised to produce further granules. The end section of the spherodizer completes drying of the product, which exits at about 90^{0}C, to be sent to the screening, cooling and anticaking sections, after which it is stored.

The standard quality of the product is as follows:

Particle Size	:	**> 4mm,**	**4-2.8mm,**	**2.8-2mm,**	**2-1mm**
		7%	**73%**	**16%**	**4%**
CRH	:	**45%-60%**			
Bulk Density	:	**1150 gr/dmc**			
Repose angle	:	**28^O**			
Moisture	:	**1.2-1.8%**			

Process energy consumption, excluding gas scrubbing, are as follows:

EE = 36 kwh/t
CH4 = 18-20 Nm^3/t

The hot gases from the spherodizers are sent by fans to a cyclone train, which almost completely separates the powder, to be sent back to the cycle, and then proceed to final scrubbing. [see figures 1 and 2]

2.2.1 SPHERODIZER OPERATION

The optimum spherodizer operation must reach two specific targets:

maximum hourly production, with the requested product particle size;

highest degree of roundness possible

Several factors affect the spherodizer performance:

a] **Quality of the granule layer**

depends on the layout of internal drum devices, as well as drum rotating speed.

b] **Granule layer density**

is a function of the slope and the charge. Therefore, the charge must be controlled by adjusting the recycle flow, which varies from 1-1.2. The recycle should be made up of small granules, which act as initiators for the next granulation process.

c] **Feed slurry quality**

depends primarily on the water content and the temperature. There is a critical moisture level, below which it is impossible to granulate. Should the moisture be excessive, the granulometric spectrum shifts towards "over size", which reduces the flow rate, which is also affected by limited drying capacity.

It is extremely important, furthermore, that the liquid spraying phase be kept constant. Therefore, if moisture decreases, it is necessary to increase the slurry flow rate in order to restore liquid phase consistency [water + soluble salts].

d] **Drying conditions**

are directly affected by the air flow rate and system temperatures. Insufficient air flow rate causes excessive growth of the product, due to increased residence times. An excessive air flow rate may shift the product layer backwards, reducing its density; furthermore, the droplet spray dries before coming into contact with the building-up granule.

The inlet temperature is set a few degrees below product melting point, which is directly linked to slurry composition, moisture and pH. This point may fall because of dishomogeneous slurry composition, high moisture levels and low pH.

2.2.2 OPTIMUM OPERATING PARAMETERS

The table below shows the optimum operating parameters [slurry moisture, flow rate and hot air temperature], which are to be maintained in order to achieve good product quality.

FORMULA	PRODUCTION TON/DAY	SLURRY MOISTURE %	HOT AIR FLOW RATE m^3/hr	TEMP HOT AIR ^oC	TEMP EXITING SALT ^oC
8-24-24	500	20-22	85000	280	90
12-12-12	525	18-20	100000	300	90
15-15-15	800	16-17	87000	280	90
20-10-10	650	12-13	90000	180	90
20-10-10- S	650	12-13	90000	200	90
23-23	700	17-19	100000	190	90
16-35	500	17-19	100000	200	90
25-10	650	12-13	90000	170	90
18-18-5	600	14-16	100000	190	90
11-22-16	650	16-18	90000	280	90
12-6-18 S	500	16-18	110000	280	90

3] EFFLUENT SCRUBBING UNIT

The scrubbing unit is fully automated, and purifies the process gases from reaction [flow rate= 25000 Nm^3/hour, T= 88^oC] and granulation [flow rate= 180000 Nm^3/hour, T= 90^oC], and reduces the atmospheric emissions of powder, ammonia, nitrogen oxides and fluorine below the legal limits in force.

Comprehensively, the maximum quantities of inlet pollutants are:

Ammonia	**860 kg/hr**
Nitrogen oxides	**20 kg/hr**
Fluorine	**5 kg/hr**
powders	**100 kg/hr**

The maximum quantities of pollutant emission to the atmosphere through the stack are:

Ammonia	**7.5 kg/hr**
Nitrogen oxides	**3 kg/hr**
Fluorine	0.3 kg/hr
Powders	**4 kg/hr**

Scrubbing performance is, therefore:

Ammonia	**99%**
Nitrogen oxides	**85%**
Fluorine	**94%**
Powders	**96%**

3.1 PROCESS DESCRIPTION

The reaction gases are scrubbed separately from the granulation gases. The first scrubbing is performed in a high pressure drop Venturi scrubber [ΔP = about 400 mm], fitted with a radial spraying system in the throat, and in column T 600 [H= 9m, D=1.5m], which is also fitted with four spraying devices and an inertial drop catcher.

The purpose is to scrub:

a] **the aerosol produced by nitrogen oxides in presence of water and ammonia;**

b] **part of the ammonia from the ammoniation reactors.**

The Venturi scrubber and column T 600 are fed with phosphoric or sulphuric acid. An optimum concentration of ammonium sulphate or ammonium phosphate for recovery in the reaction step is achieved by utilising an automatic densimeter.

3.1.1 UTILISATION OF SULPHURIC ACID

Acid is automatically fed by a pH controller, set to 1.5.

The density of the resulting solution is controlled by a continuous density detector, which activates the recovery acqueous flow inlet, ensuring that the density is in the range of 1350 to 1400 kg/m^3, in order to optimise the quantity of ammonium sulphate solution to be recovered, which will have a concentration of 37–40%.

3.1.2 UTILISATION OF PHOSPHORIC ACID

The total requirement of acid necessary for the specific grade under production is charged. The charged quantity is such that the resulting weight ratio N/P205 is always below 0.12, since it is well known that with higher values, ammonium phosphate solubility is drastically reduced [see attached diagrams, fig. 3, 4, 5, 6, 7]. Consequently, the pH controller is deactivated, whereas the densimeter, which works as a function of temperature, remains activated, to avoid physical conditions which favour crystallisation. [2]

In order to guarantee long material life, and to limit operating temperature to 95°C, phosphoric acid is diluted in tank V602 with a washing solution from tower T601, bled from pump P604 delivery.

3.1.3 After scrubbing, the reaction gases still contain fluorine, and part of the ammonia. They are mixed with the granulation gases, which contain powders and ammonia which is released from the product during drying. All the mixed gas undergoes further treatment, divided into three phases.

a] **Basic Scrubbing**

This phase comprises two saturators and average pressure drop Venturi scrubbers [ΔP= about 200 mm], installed in parallel, followed by column T601. The Venturi scrubbers feature radial spraying in the throat, and a pressure drop adjustment system controlled by a single servomotor. Tower T 601/T 602, height = 23m, diameter=3.8m, comprises drop separators and a separation system between the trays to catch the liquid sprayed into the acid washing section by means of a battery spraying system. The pH is kept in the range 4.5-5.5 by the high quantity of ammonia present in the granulation gas. During this treatment phase, the powders and the fluorine are scrubbed. The resulting solution is mixed with the solution from the first section, and is then recovered in the reaction step.

b] **Acid Scrubbing**

The gas from the basic treatment flows through T 602, where all residual ammonia is scrubbed. Absorption is by means of a strong sulphuric acid solution [pH= about 3], automatically metered by a pH-meter, with a reflux which makes it possible to concentrate the ammonium sulphate solution obtained so that it can be recovered in reaction.

The concentration of the above-mentioned solution is adjusted by a densimeter, which controls the addition of water from the following wash.

c] **Final Scrubbing**

The final scrubbing is performed in column T603, with industrial water, so as to scrub all droplets of ammonium sulphate eventually present in the gas due to mechanical entrainment, by means of tangential gas inlet, and a droplet catcher. The purified gas, saturated at 50-55°C, exits to the atmosphere at a height of 60m. The process, utilising the spherodizer gas saturation heat, favours partial evaporation of the water in the scrubbing solutions, thereby reducing to zero the plant liquid discharge [see figure 7].

The scrubbing plant EE consumption is 18 Kwh/T.

3.2 CHOICE OF MATERIALS

Particular care was taken in choosing the construction materials, in view of the excessive corrosive behaviour of the fluids, due to the high level of acidity in the presence of chlorine and fluorine ions, and highly abrasive powders. All gas pipings are made from polyester resin, reinforced with fibreglass. The liquid pipings are made of PVC or PP, reinforced with SVR, except for certain sections exposed to the worst conditions, which are made of Hastelloy C. The columns are made of polypropylene, reinforced with fibreglass, whereas the pumps in contact with highly abrasive acid solutions are made of HDPE.

The fan impellers are made of URANUS B 6 [F600] AISI 316 L [F601], casing in carbon steel, clad with butyl rubber.

The Venturi scrubber for the first acid wash is in polypropylene, reinforced with fibreglass.

The Venturi scrubbers for the basic wash are in carbon steel, clad with butyl rubber. The latter are to be replaced with scrubbers in polypropylene, reinforced with fibreglass, due to the severe corrosion and erosion phenomenons observed.

REFERENCES

[1] OPERATING HANDBOOK FROM PEC [1975]

[2] MANUAL OF FERTILIZER PROCESSING ed FROM NIELSSON

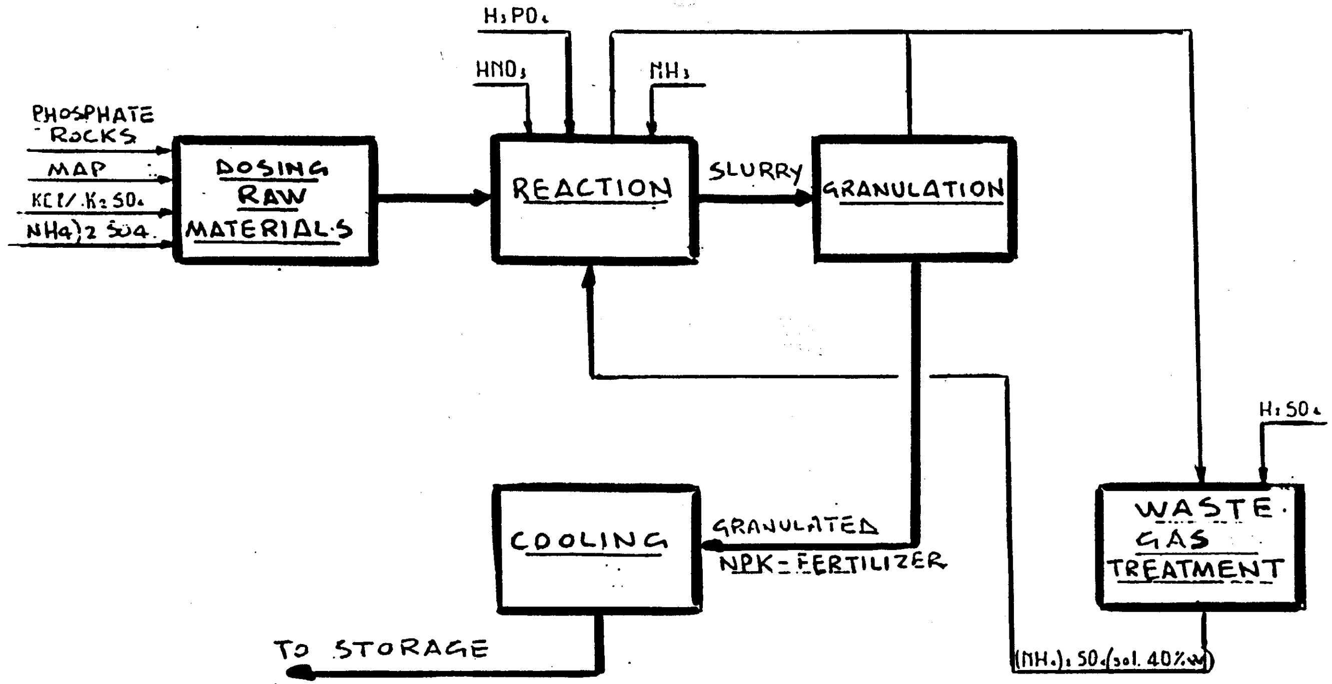

Fig. 1

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BLOCK DIAGRAM

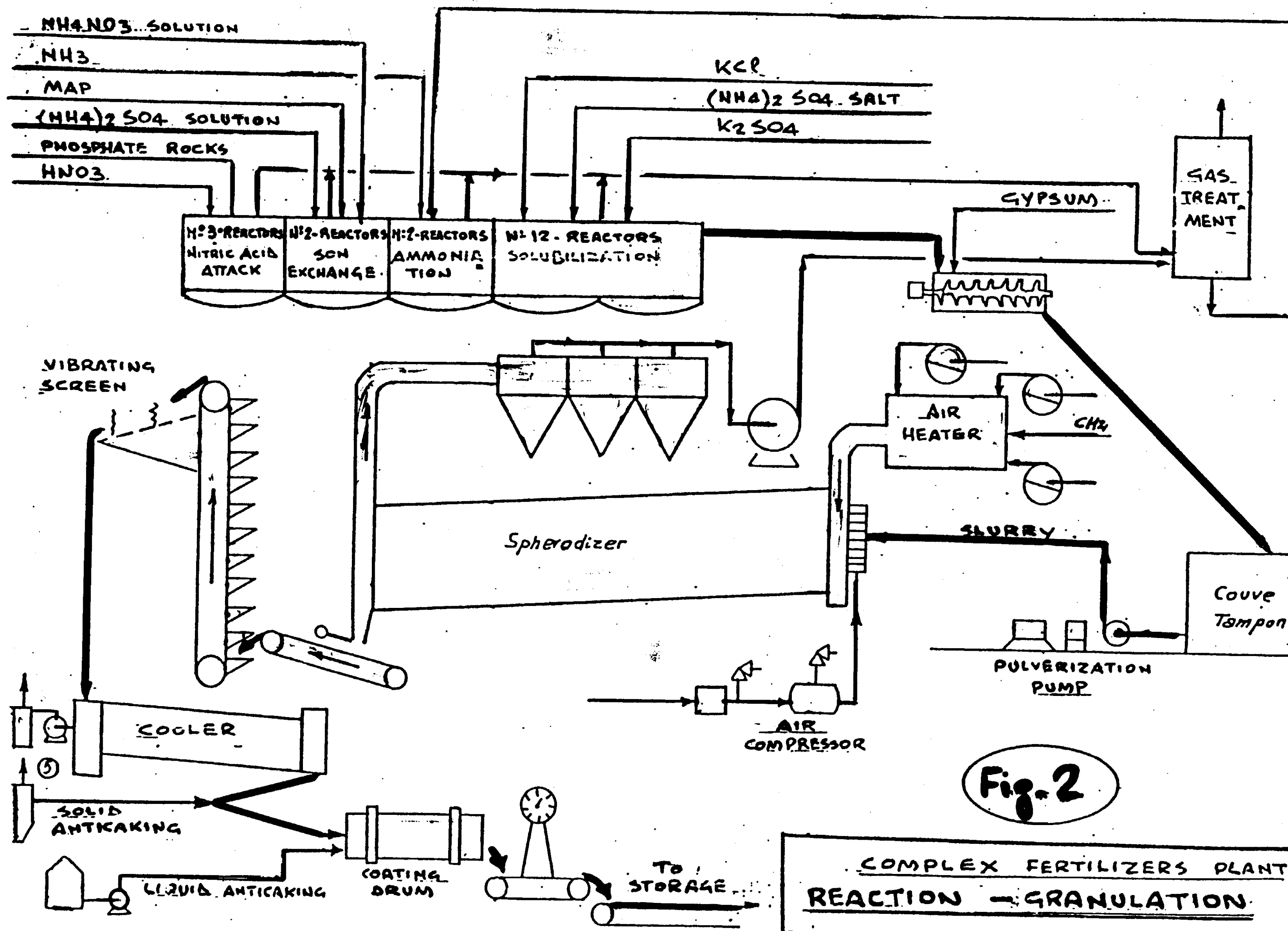

Fig. 2

COMPLEX FERTILIZERS PLANT

REACTION - GRANULATION

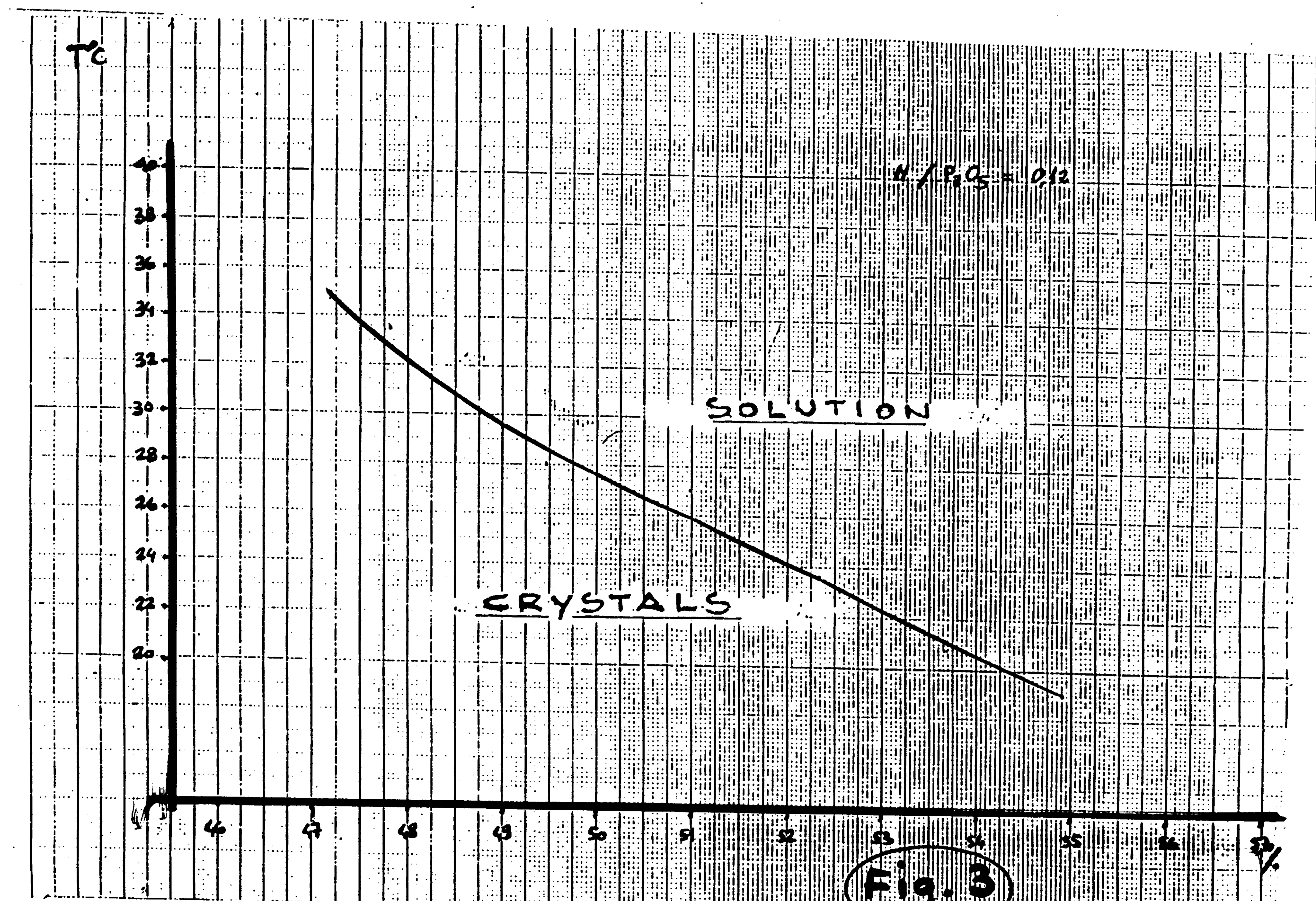
T°C
40
38
36
34
32
30
28
26
24
22
20
46
47
48
49
50
51
52
53
54
55
56
57 %
SOLUTION
CRYSTALS

Fig. 3

SOLUBILITY OF SATURATED AMMONIUM PHOSPHATE SOLUTION

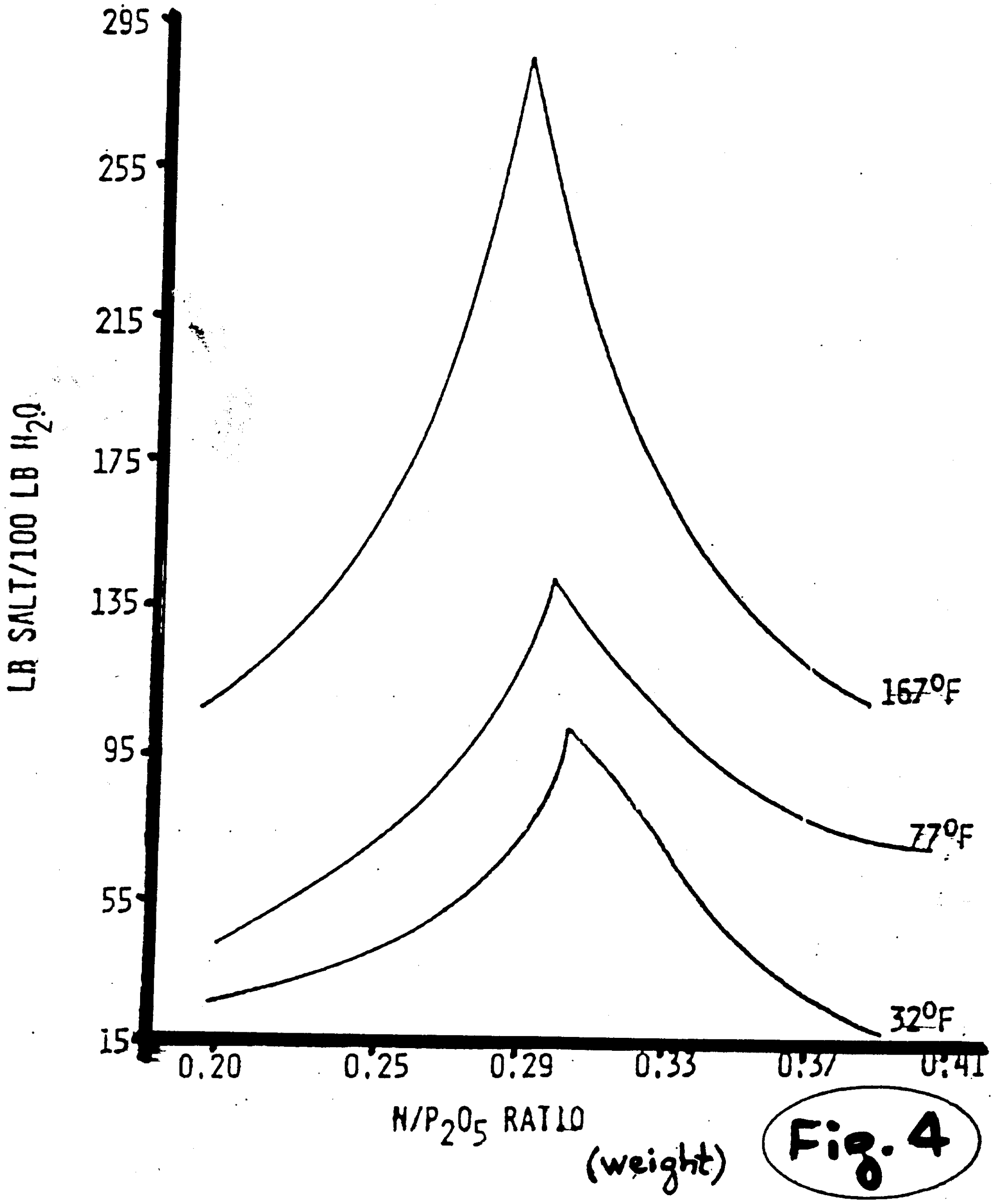

Fig. 4

SOLUBILITY OF SATURATED AMMONIUM
PHOSPHATE SOLUTION

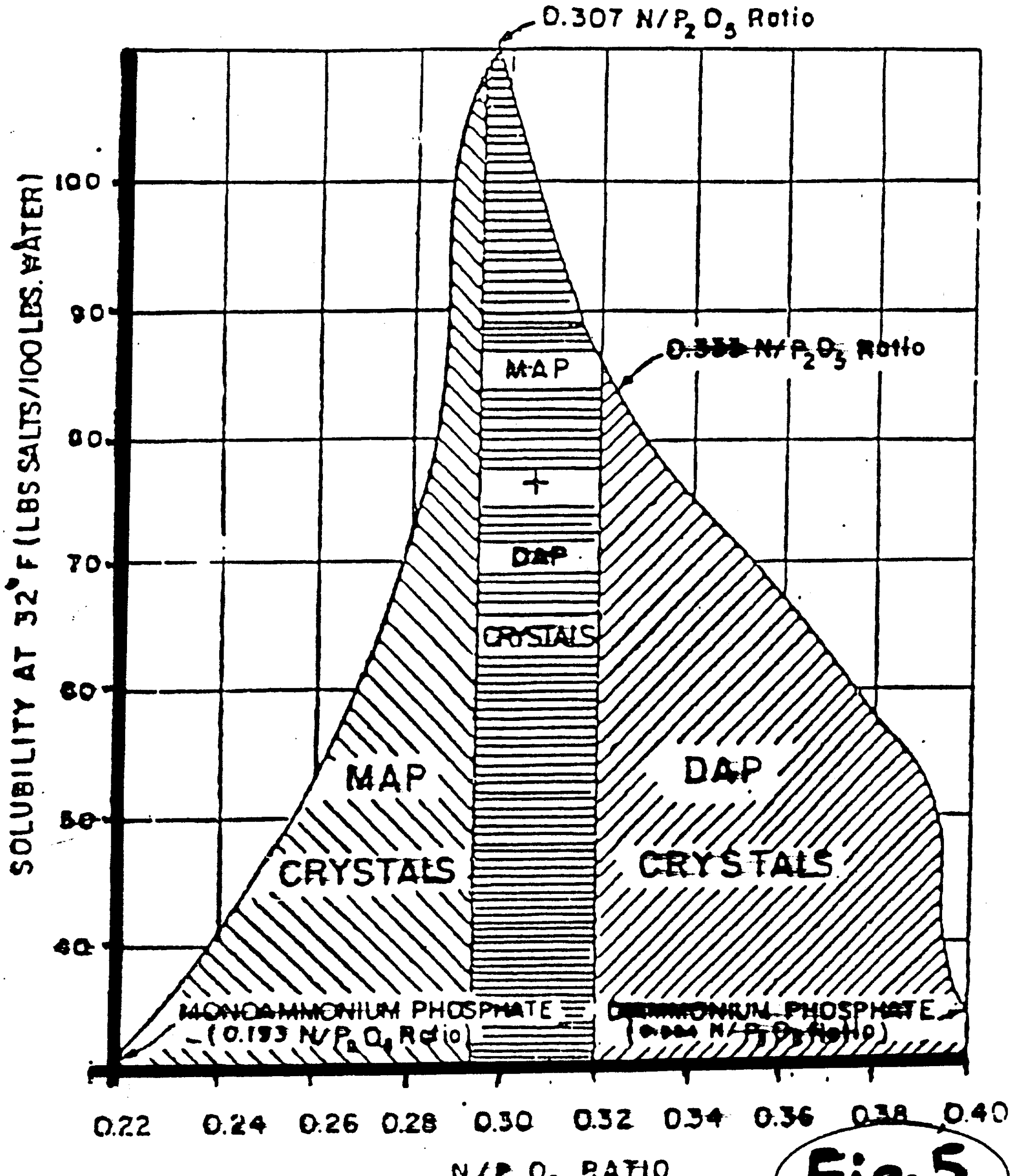

Fig. 5

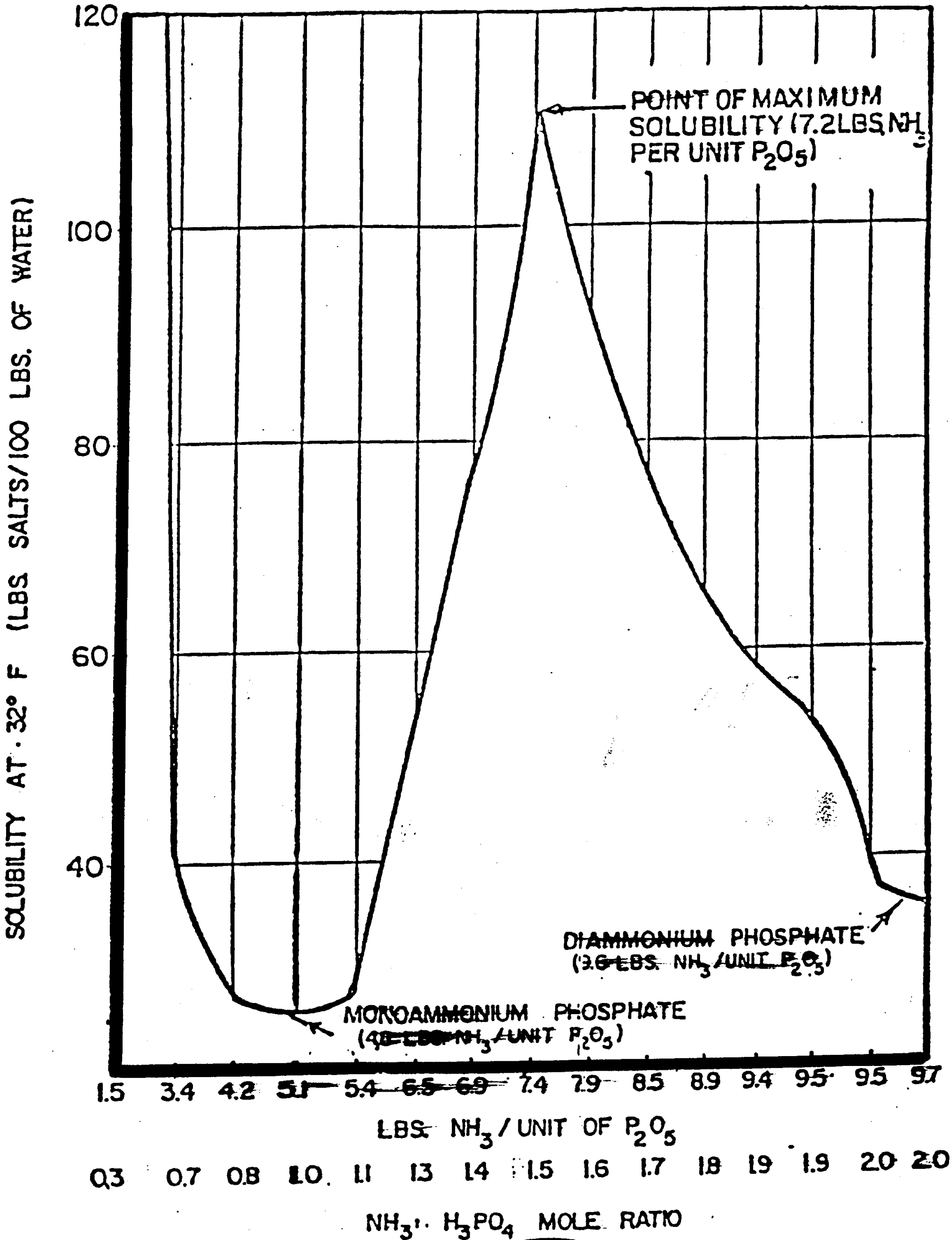

FIG. 6

SOLUBILITY OF SATURATED AMMONIUM PHOSPHATE SOLUTIONS

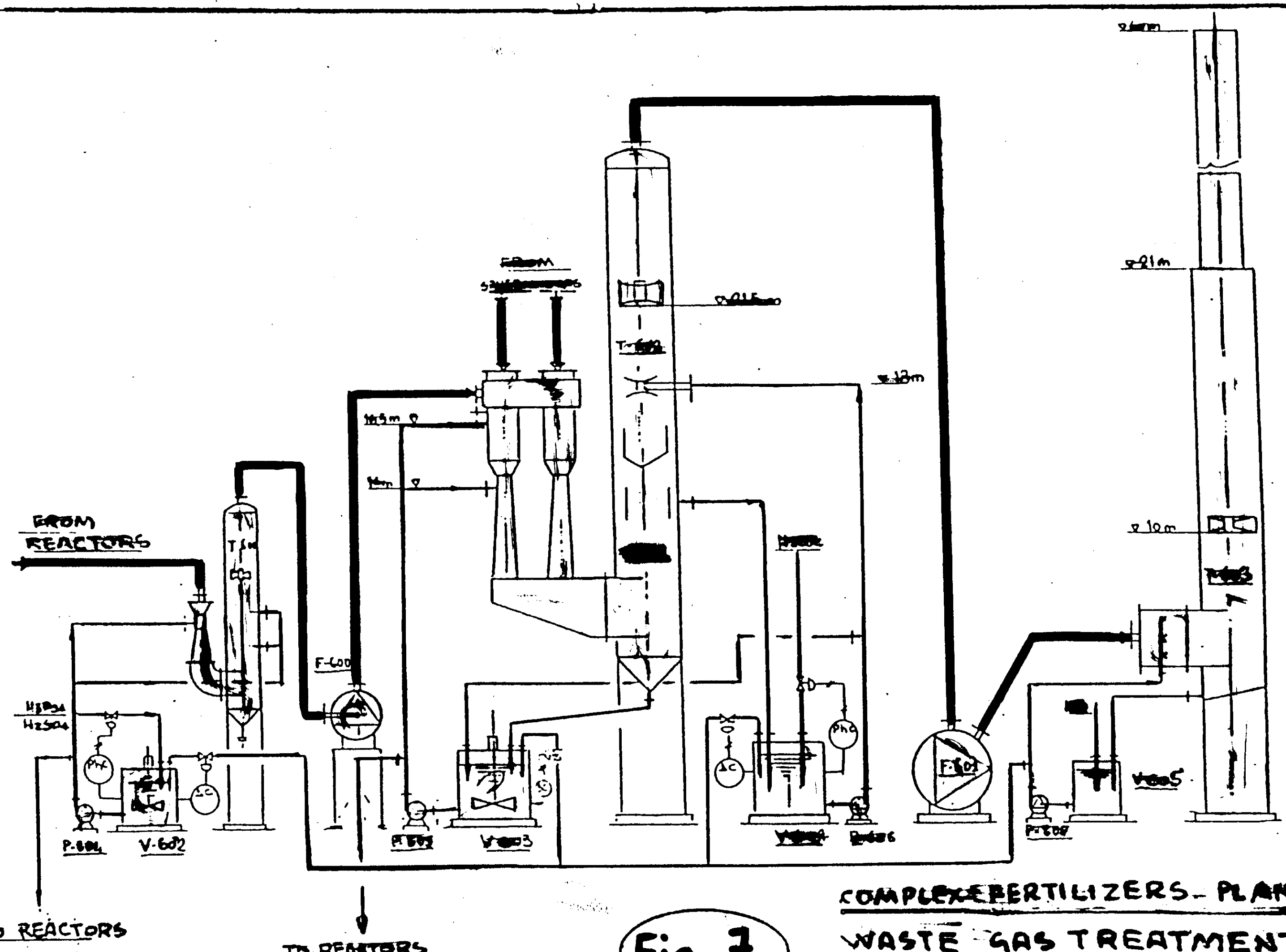

Fig. 7

COMPLEX FERTILIZERS PLANT
WASTE GAS TREATMENT