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AMMONIUM SULPHATE IN THE PRODUCTION OF NITROPHOSPHATE

by

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SUMMARYAMMONIUMSULPHATE IN THE PRODUCTION OF NITROPHOSPHATE

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The world output of ammoniumsulphate is, to a large extent, derived as a by-product co-product. It can be used as calcium precipitant in a nitrophosphate process.

In this process the solution obtained after acidulation of phosphate rock with nitric acid is treated with ammonium sulphate.

The calcium is precipitated and removed as gypsum.

When producing, for instance, 80 per cent water-soluble P_2O_5 in the end product, all of the dissolved solution, together with the ammoniumsulphate, is fed to the precipitation section. The precipitation conditions are chosen in such a way that a gypsum is obtained which can be filtered easily.

The filtrate is collected and fed to the neutralization and evaporation sections.

The neutralization, being a delicate part of the process, is very well controlled by automatic pH control. The evaporation poses special problems, due to the nature of the products, for these materials have a boiling point which lies below the crystallisation point of ammonium phosphate at concentrations of over 80 per cent.

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Depending on the method of obtaining the end product, evaporation is carried out to 99 per cent for prilling and to 95 per cent for granulation.

Which of these methods should be chosen strongly depends on the prevailing situation and on the product desired.

Usually, for high capacities of between 700 and 1800 tons, with only a few grades being wanted, the prilling process offers more economic advantages. For lower capacities, with a greater variety of grades, the granulation might be chosen.

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We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

The use of ammonium sulphate in the production of nitrophosphates:
the Stamicarbon process

1. Introduction

Why ammonium sulphate as a raw material?

The consumption of ammonium sulphate as a straight fertiliser shows not only a relative, but also an absolute decrease.

The product can be bought at world-market prices, which often only cover the transport costs, while the nitrogen and sulphur are free.

If ammonium sulphate is considered as a raw material for high-nutrient compounds it is worthwhile to investigate how this situation shall be continued.

The greater part of the world output of ammonium sulphate is obtained as a caprolactam (raw material nylon) co-product, in most cases 4.5 tons of ammonium sulphate is produced per ton of caprolactam.

Some processes are available which produce less ammonium sulphate, e.g. Stamicarbon's new Nymphosphate process, which yields only 1.8 tons of AS per ton of caprolactam, and BASF's process, producing 2.6 tons of AS per ton of caprolactam.

Today's caprolactam production amounts to 1.5 million tons, giving 6 million tons of ammonium sulphate.

For 1974 a caprolactam production of 2,000,000 tons is envisaged, giving a production of around 7 million tons of ammonium sulphate (see Fig. 1).

The conclusion might be that there is a tendency towards a lower ratio of ammonium sulphate to caprolactam, but with the existing production units the average will be somewhere around 2.5 tons of ammonium sulphate per ton of caprolactam. This puts a stop to the increase of the ammonium sulphate production, which will level out at 7-8 million tons per year. The consumption of ammonium sulphate will reach a level of 3.5 million tons per year in 1975 (present consumption about 5 million tons).

From the above considerations it is seen that ammonium sulphate can be used very well as a raw material.

11. The Stimulation process for the production of superphosphate with high water-soluble P_2O_5 content

Although having at its disposal an OXDA-type calcium-nitrate crystallisation process, DSM largely turned to the precipitation process. We shall now review, step by step, the most interesting parts of the process.

1. Digestion section

The digestion of the phosphate rock can be done with 9-10 % less nitric acid than would be needed if equimolar ratios had to be used. This is in contrast with the crystallisation process, which requires an excess of nitric acid of up to 25 % (most of which later on appears as ammonium nitrate) to obtain a 20-20 material of 80 % water-solubility.

The main reactions which occur in the digestion stage are:



If the above-mentioned convenient $NO_3/N/P_2O_5$ ratio is used, the minimum N/P_2O_5 ratio of the product will be around 1.4, depending to some extent on the type of phosphate rock and desired water-solubility (see Fig. 1).

2. Precipitation and filtration section

An ammonium sulphate solution and the digested rock solution are fed to the first precipitation reactor, in a certain ratio.

The addition of the sulphate has to be done carefully, in such a way that an easily filterable precipitate is obtained. It is, of course, possible to bind almost all the calcium ions as calcium sulphate, in which case the filtrate, after proper treatment, yields 80-100 % water-soluble ammonium phosphate.

If a different water-solubility is preferred, part of the digestion liquid can be short-circuited around the precipitation, which means that the final solution

will contain the desired amount of calcium phosphate. In this way the water-solubility of the final product can be controlled as desired.

The main precipitation reactions are:



The slurry, containing the gypsum as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is continuously fed to a tilting pan filter, via a second reactor.

The filtration, which is completed in one revolution of 360°, can be divided into the following stages:

- first filtration
- 1 or 2 washings of the gypsum cake
- drying of the cake by suction
- removal of the cake.

The easy filterability is shown on the next two slides. Slide 1 shows that the product is almost dry after the first pan; slide 2 shows that the gypsum is easily removed. A special type of filter cloth has to be used during this operation.

3. Neutralisation and evaporation

The collected filtrate is neutralized with ammonia. This is a delicate process step, because in the production of fertilizers of lower water-solubility too high a pH value will cause formation of tricalciumphosphates, which normally results in a lower water-solubility - as wanted -, but also influences the citrate-solubility.

On the other hand, if NPK is produced with ECI in the last stage of the process too low a pH value may facilitate decomposition of the product in stock.

The neutralisation reaction is exothermic and, depending on N/P₂O₅-ratio and water-solubility, boiling in the neutralizer is possible.

The main neutralisation reactions are:



The proper degree of neutralisation is obtained by automatic pH control.

After neutralisation, the solution has to be concentrated. The evaporation of water also presents some special problems in this case. In the first place this is due to the fact that within a wide range of concentrations the boiling point of the mixture is under the crystallisation-temperature of ammonium-phosphate (Fig. 3) In the second place difficulties may be caused by the presence of gypsum if a product of lower nutrient value is desired.

A circulation-type evaporation, however, gives very good service for this purpose. A two-stage unit is chosen for reasons of economy. In the first stage the solution is concentrated from 50% to 75% at a boiling temperature of about 120 °C. In the second-stage evaporation the temperature of the circulating melt is about 170 °C, and is kept well above the crystallisation point.

The melt is now ready to receive its final form. A selection can be made out of two methods: prilling or granulating.

4. Shaping

For capacities over 700 metric tons/day, the capital investment will be lower for a prilling plant than for a granulation plant. For a production of approx. 1000 tons/day, the difference is in the order of 20%. The power consumption and heat requirements are more favourable in the prilling operation (compare removal of water out of a melt and out of a solid granule). Another great advantage of prilling is the simple operation and the smooth running of the plant. The recycle will be about 10%, whereas with a granulation operation it might rise to 400%. However, there is a limit to the composition of compounds to be prilled. Materials with a high viscosity and a high percentage of solids in the melt (for instance NPK's with a low N to P₂O₅-ratio and a high KCl-

content) may pose problems in prilling. For more detailed information I refer to other sources (Lit. 1, 2, 3).

III. Economics of the process

Comparisons for grass-root plants based on different processes have been made on several occasions (Lit. 4, 5, 6).

We will here restrict ourselves to dealing with a special case where a fertilizer production unit is available.

Starting from the fact that the existing production is based on phosphoric acid and nitric acid, we will look more specifically at extension of such a plant with a nitric acid digestion and precipitation-filtration stage.

It will be clear that the decision to rebuild is largely dependent on the price of ammonium sulphate.

It does not matter whether phosphoric acid has to be bought or is produced by the same company. In the first case the purchase price has to be considered, in the latter the sales price.

For ease of calculation, only one product (viz. 17-17-17) and one capacity (600 tons/day) will be considered.

Table I gives the cost prices of the product based on the two different production methods.

Table II gives the total out-of-pocket costs, including the difference in manpower requirements and maintenance.

The difference in cash-flow can be calculated from table II; it amounts to $C = 200,000 (-3.70 + 0.112 Y - 0.37 X)$.

This relation is presented in Fig. 5, for different P_2O_5 -prices, as a function of the ammonium sulphate price.

The graph is helpful in estimating the ammonium-sulphate price, if a certain profit on new investment is demanded.

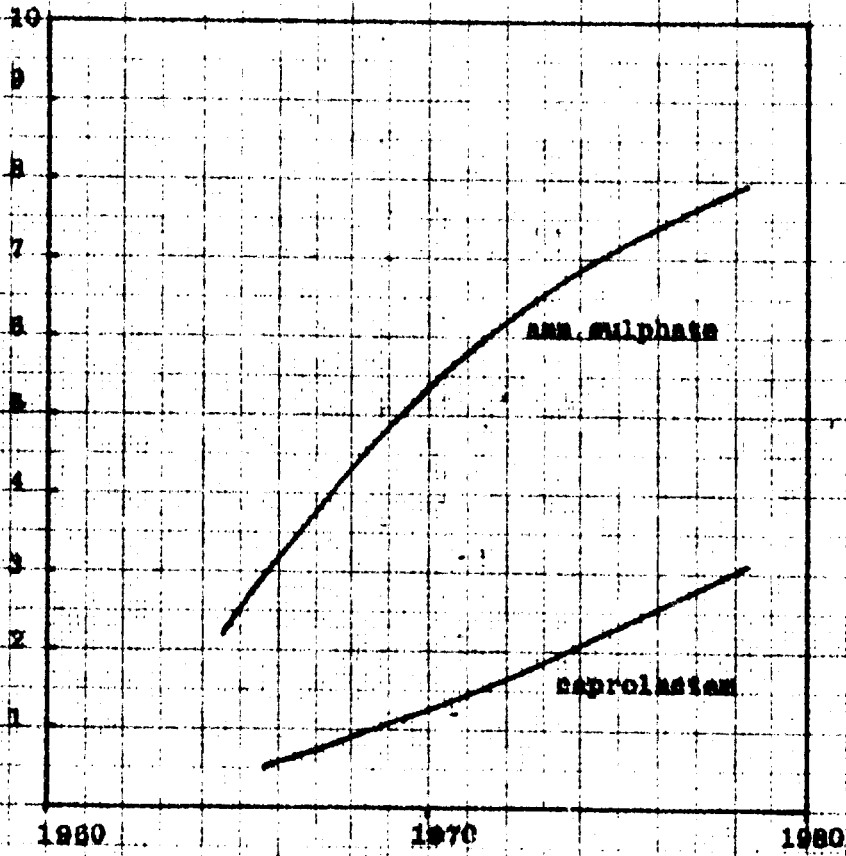
For example, if the DCF (based on 10 years, before taxation) on new investment has to be 15%, the minimum cash-flow for an investment of \$ 3.5 mm has to be \$ 100,000 per year. For a present phosphoric-acid price of \$ 130 per ton of P_2O_5 , the ammonium-sulphate price has to be maximum \$ 20 per ton C.I.F.

This means that a fertilizer producer, now using phosphoric acid and in a position to buy ammonium-sulphate at a price lower than \$ 20 per ton, can realize a profit of at least 15% on his new invested capital.

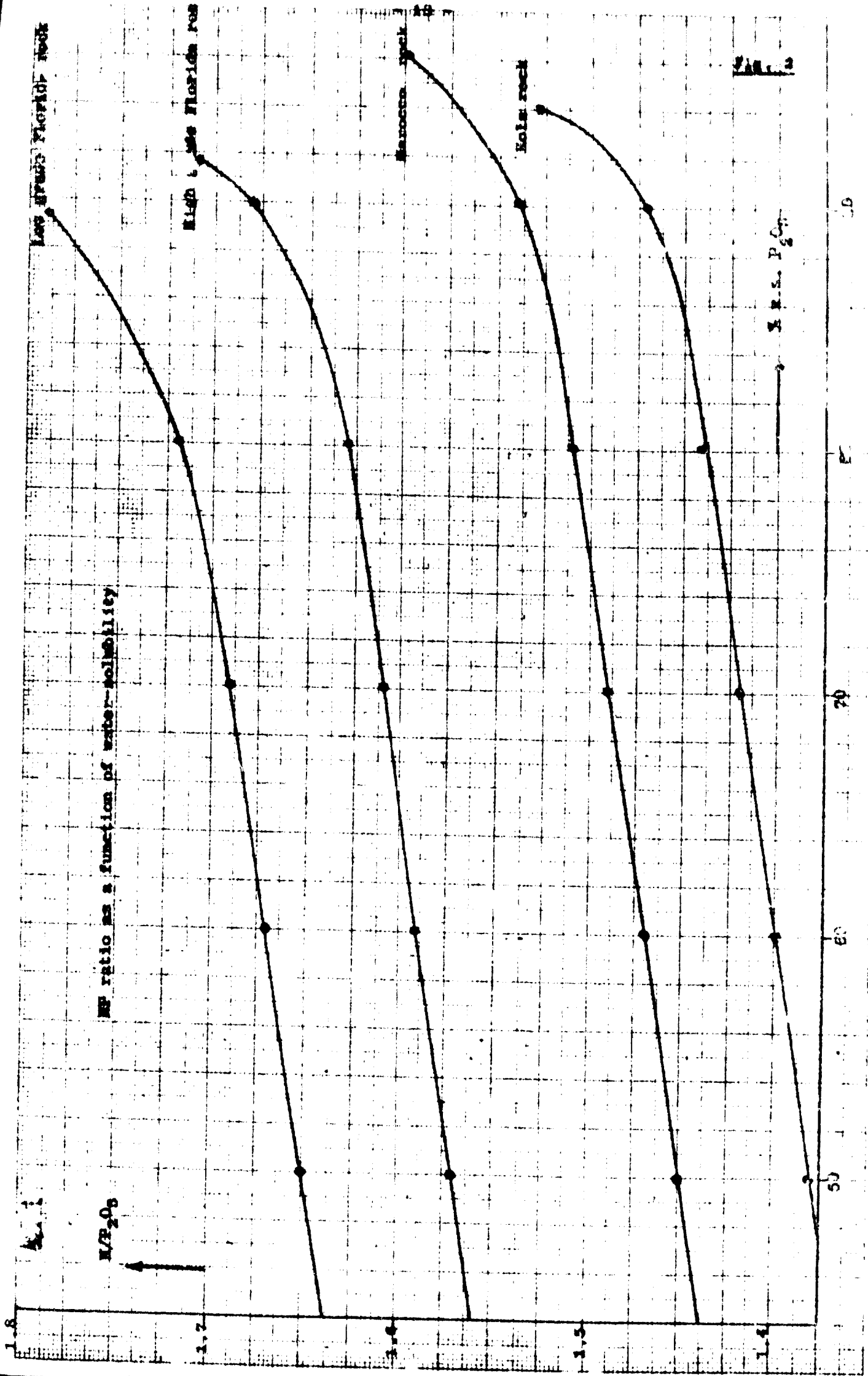
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Mitchell, D.A. Indian Chem. Journ. December 1967

Production in
 10^6 ton

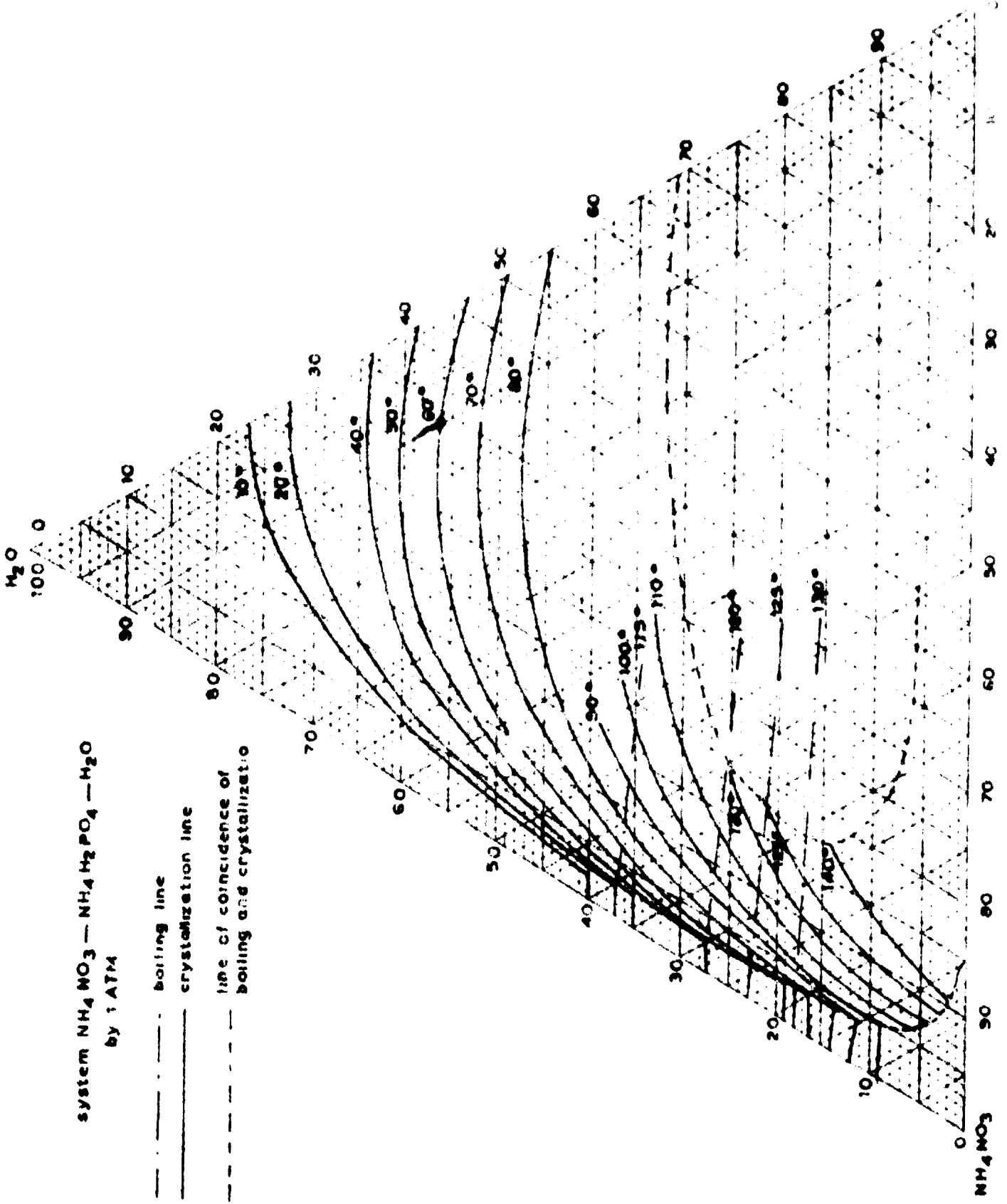


Production of ammonium sulphate from caprolactam

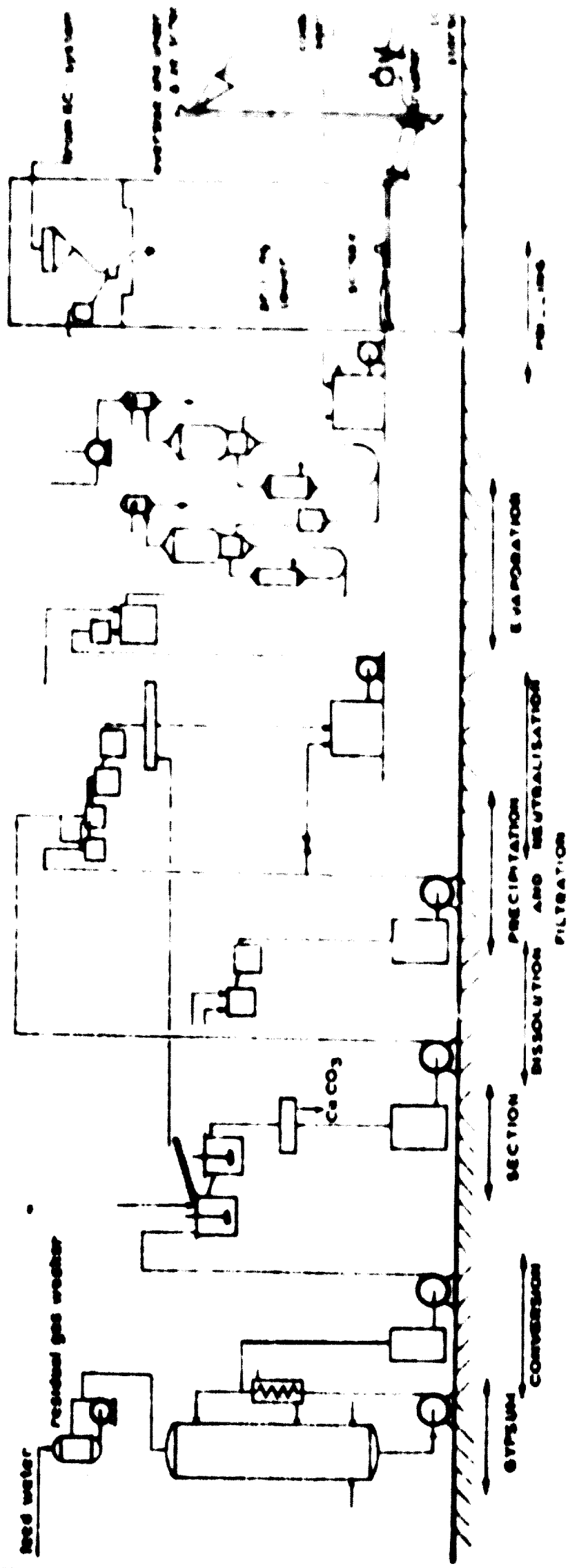


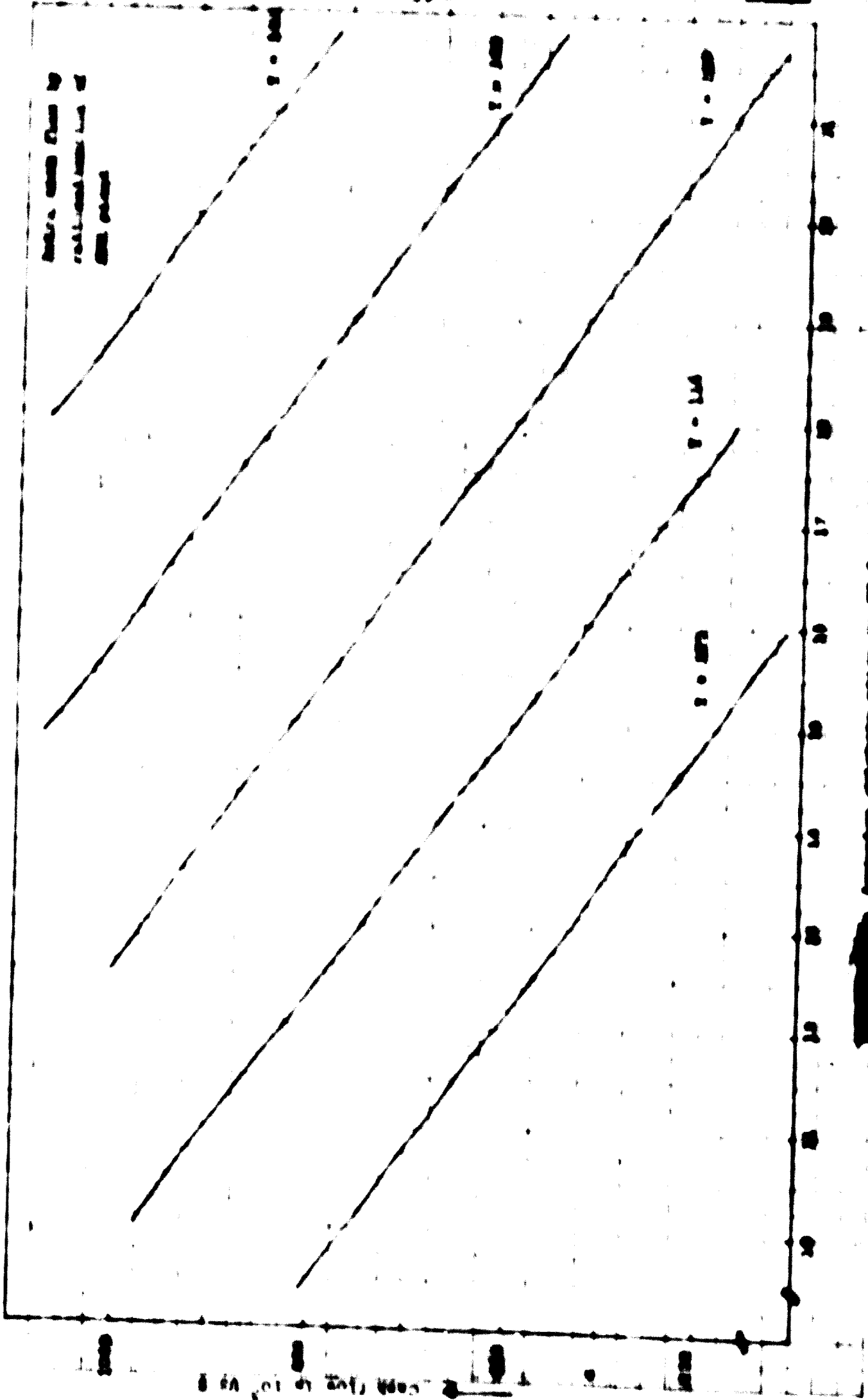
system $\text{NH}_4\text{NO}_3 - \text{NH}_4\text{H}_2\text{PO}_4 - \text{H}_2\text{O}$
by 1 ATM

- boiling line
- crystallization line
- - - line of coincidence of boiling and crystallization



FLOW-SHEET NP OR NPK PRODUCTION WITH
REMOVAL OF CALCIUM BY PRECIPITATION





1.00
1.05
1.10
1.15

...

Table II

Cost-flow rationalization for 200,000 units

	Phosphoric acid process cost in \$ per ton	Phospho-nitro process cost in \$ per ton
Appr extra investment	-	3.5 MI
Variable cost price	19.30 + 0.176 Y	23.00 + 0.064 Y + 0.37 X
P ₂ O ₅ price = Y \$/ton		
X price = X \$/ton		
Extra operation (2 operators)		0.10
Extra maintenance		0.65
Total out-of-pocket costs	19.30 + 0.176 Y	23.00 + 0.064 Y + 0.37 X





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