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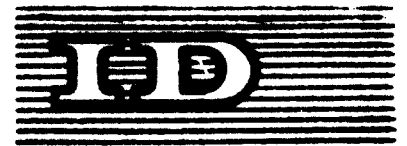
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Second Interregional Fertilizer Symposium

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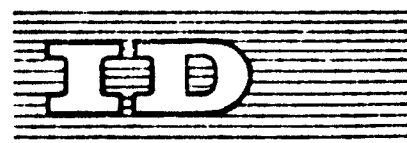
LIQUID FERTILIZER PRODUCTION AND DISTRIBUTION^{1/}

by

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SUMMARY

LIQUID FERTILIZER PRODUCTION AND DISTRIBUTION

by

Travis P. Mignett

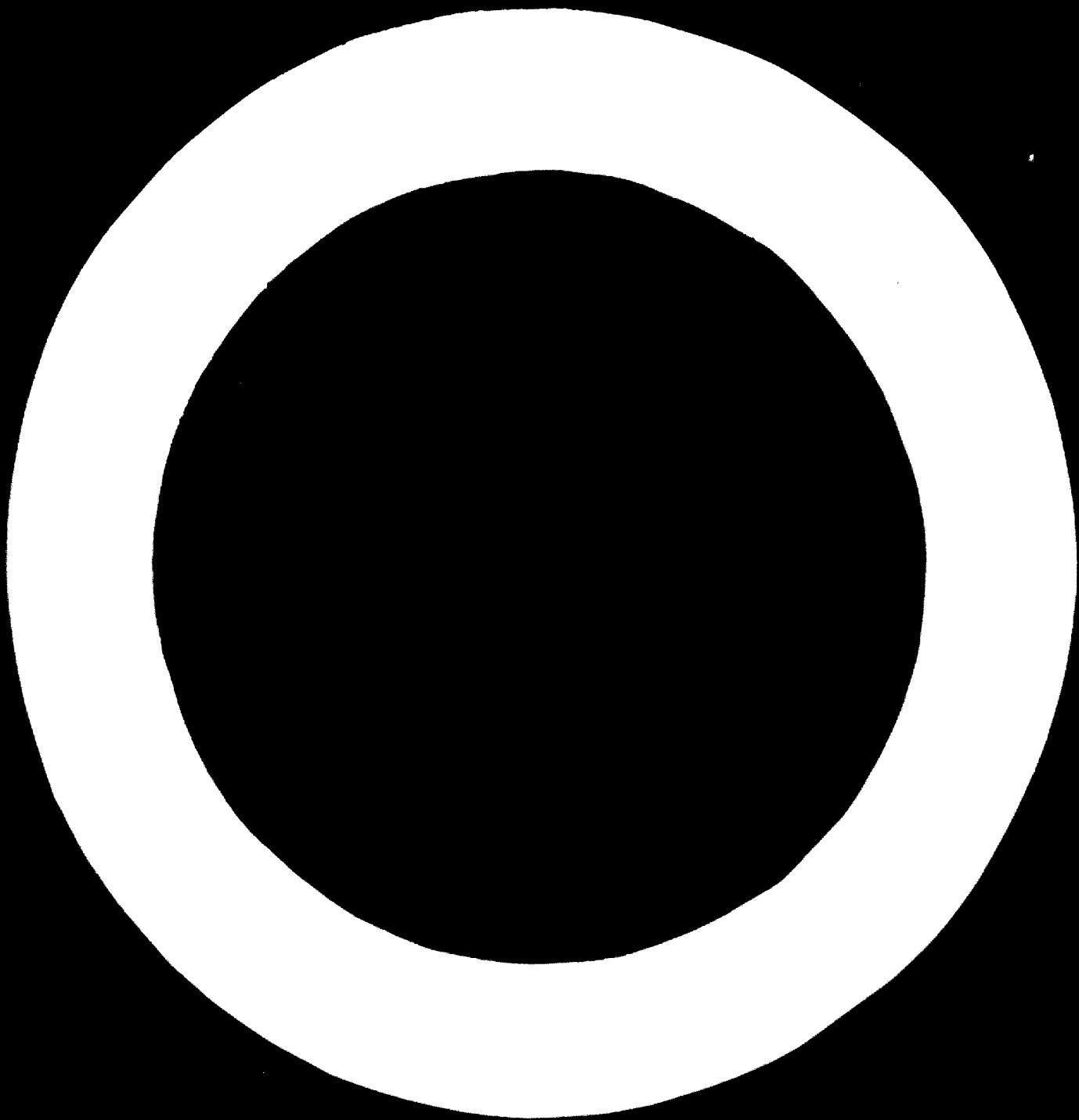
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The use of liquid mixed fertilizers and nitrogen solutions is increasing rapidly in the United States. Many farmers prefer liquids because of convenience, ease of application, and adaptability to precise, uniform placement. Both farmers and manufacturers benefit from the absence of caking, dustiness, hygroscopicity, and inhomogeneity. Manufacturing processes are simple and inexpensive. Problems of fume and dust are absent. Storage and handling costs are lower for liquids than solids. Investment in production facilities for finished products is low.

Although liquid mixed fertilizers are less concentrated than solids, transportation costs are minimized by shipping highly concentrated intermediates to small, local plants which make the final products, often by custom mixing for crops and soils in local areas. The production and distribution pattern seems to be favorable to marketing.

Liquid fertilizers often are applied by injection in irrigation water. Combinations of liquid fertilizers with herbicides, insecticides, or micronutrients are popular. These practices are popular because of decreased requirements for farm labor and versatility of formulation.

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Liquid fertilizer use in the United States is estimated to constitute about 25 per cent of the total tonnage or about 30 per cent of the total N, P_2O_5 , and K_2O this estimate includes anhydrous and aqueous ammonia, other nitrogen solutions, and liquid mixed fertilizer.

Ammonium polyphosphate solutions prepared by ammoniation of electric-furnace or wet-process superphosphoric acid are key phosphatic materials in liquid fertilizer manufacture. Solid ammonium polyphosphate may become an important material for liquids in the future.

Suspension fertilizers -- saturated solutions containing suspended solids -- are the newest form of liquids and are likely to grow rapidly because of advantages of higher analysis, favorable economics, and greater versatility of formulation. The main disadvantage is that storage, handling, and application of suspensions are not as simple as with clear liquids.

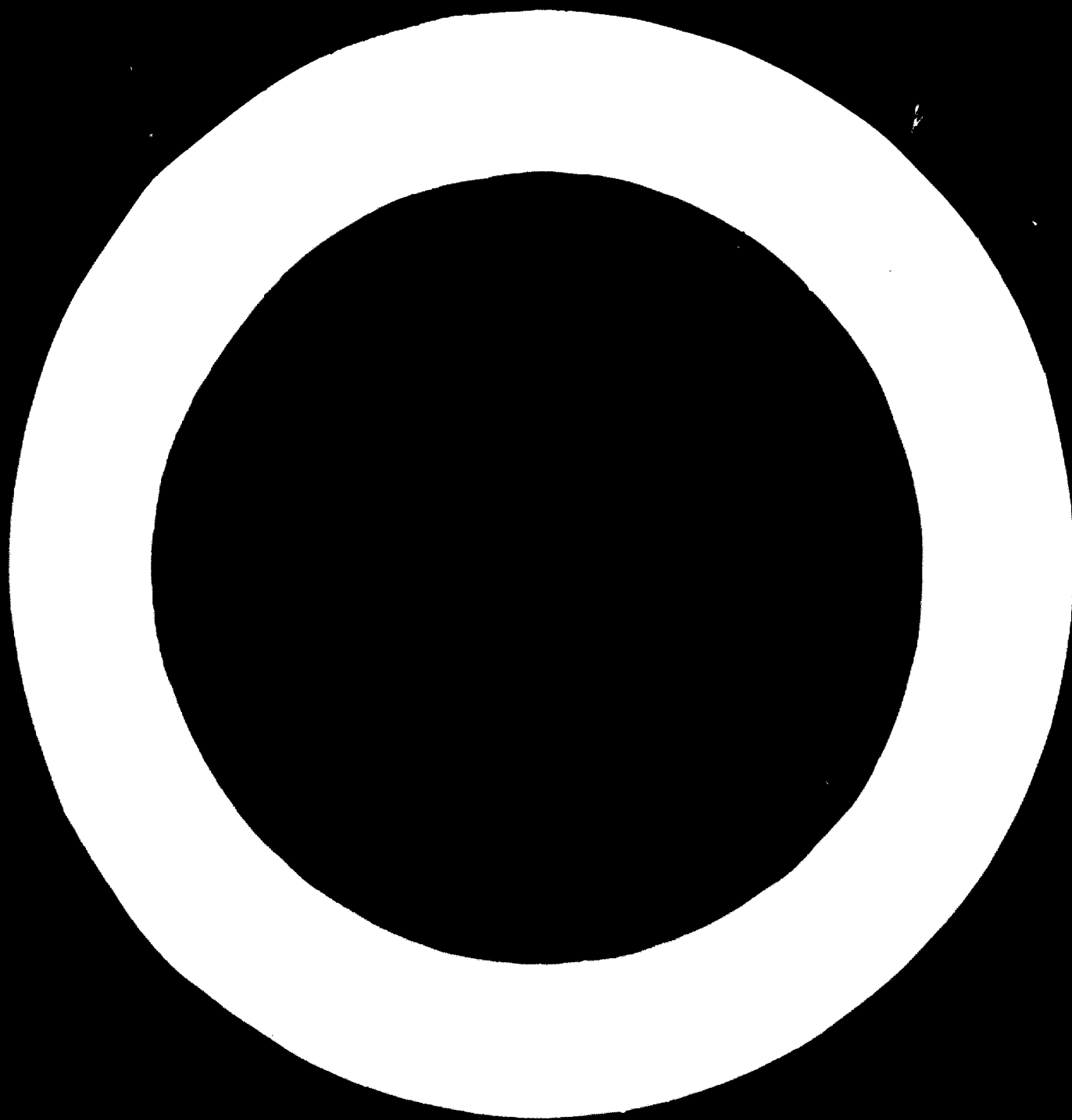
The technology of manufacturing nitrogen solutions and liquid mixed fertilizers is reviewed. As superphosphoric acid and ammonium polyphosphate solutions are key ingredients in liquid mixed fertilizers, their properties and technology of manufacture are covered in some detail. Current annual production rate of superphosphoric acid is estimated at about 600,000 metric tons of P_2O_5 in the United States. "Direct" processes that produce ammonium polyphosphate (solution or solid) without the intermediate production of superphosphoric acid are coming into industrial use in the United States and France. This development holds promise of significantly lowering the cost of ammonium polyphosphate.

The growth of liquid mixed fertilizers in USA is particularly interesting since it has resulted from the demands of farmers and the efforts of small industries rather than planning by major industrial companies or Government agencies. Industry is responding to the demand for good-quality phosphatic solutions, and an ample supply is now becoming available. There is much interest in further improvement in quality by partial purification of wet-process phosphoric acid and other methods for dealing with troublesome impurities. Supplies of nitrogen solutions and fully soluble potash salts are abundant.

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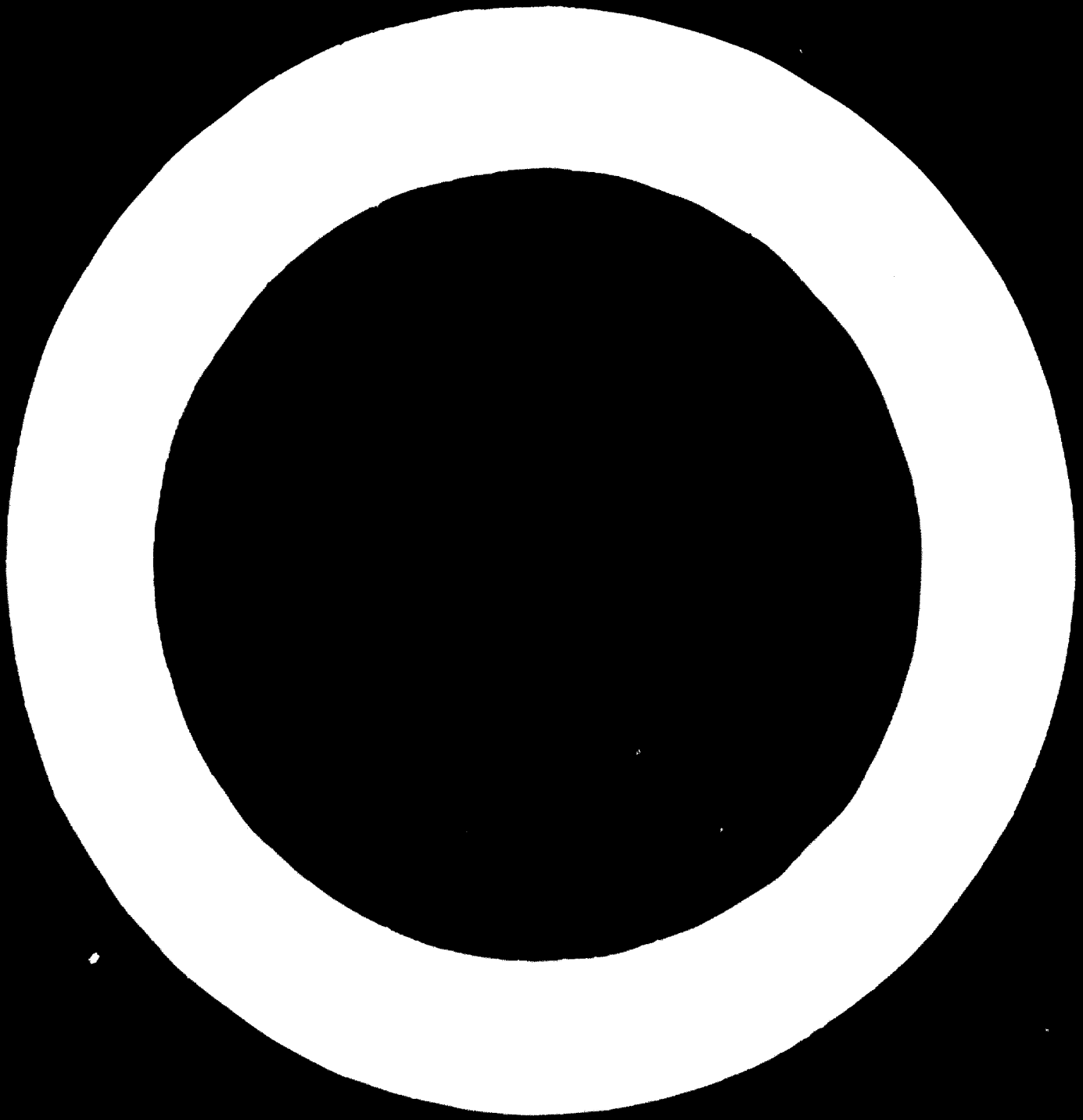
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I. INTRODUCTION

The tendency of producing concentrated, complex fertilizers brought into existence the production of several types of nitrophosphates in Czechoslovakia. Most advantageous of which, as far as economy as well as the quality of the product are concerned, proved to be the modification of the Odda process, i.e. separation of Ca-ions from the slurry obtained by nitric acid attack of phosphate rock by cooling and separation of the obtained crystals of calcium nitrate tetrahydrate (CN₄). Modification of the process consists in substituting the indirect cooling of the slurry through cooling surfaces by direct heat-transfer, i.e. by mixing the slurry with undercooled liquid heat-transfer medium insoluble in the slurry. Application of this modification brought the crystallization process qualitatively from the base of a semi-continual process with high demands on service and investment into the level of a continuous fully automatic process with high technical and economic parameters. In this way crude phosphoric acid with concentration of 30 - 34 % P₂O₅ can be practically obtained.

After pilot plant tests a production unit was constructed at Severoceske Chemické Závody (SCHZ) Lovosice and started in 1967 with a capacity of 100 t P₂O₅ per day. This unit, equipped with a single stage crystallization, operates in connection with classical granulation and produces mostly NPK fertilizers e.g. 13-19-10 with a 60 % P₂O₅ water solubility, utilizing Kola-phosphate as raw material. This year another plant with a capacity of 60 mtpd P₂O₅ has been brought into operation, which processes Morocco-phosphate. In this plant a two stage crystallization, connected with the classical granulation and carboammoniation, is used. Alternatively fertilizers 12-24-12, 16-16-16, 12-12-24 with 80 % of water soluble P₂O₅ are in production.

II. DIRECT COOLED CONTINUOUS CRYSTALLIZATION (CHP-SCHZ PROCESS)

1. Outstanding features

1.1 Direct heat-transfer

Quick fouling of heat-transfer surfaces with crystals and accordingly quick decrease of the heat-transfer coefficient present the biggest problem of the indirect cooling of acidulation slurry. It is possible to reduce a little the fouling of heat-transfer surfaces by special constructional or process adjustments, i.e. at the cost of increased utility consumption, increased investment costs, and complicating the equipment and its operation. However, fouling of the surfaces is never eliminated completely and they need to be cleaned in relatively very short intervals by defrosting.

These difficulties do not exist in the direct heat-transfer method utilizing a heat-transfer medium insoluble in the liquid to be cooled. In this case operating periods of crystallizers are very long and exceed those of the granulation section. Heat-transfer is constant during the whole operating period.

Heat losses resulting in the course of cleaning of heat-transfer surfaces by defrosting are completely eliminated.

1.2 Simplicity and reliability

The whole unit, i.e. crystallization, separation and melting of CN_4 , works completely continuous. The process is stable, the change of technological parameters and interference to the process are performed practically only with the change of raw materials of the required product quality. The product is homogenous and product quality constant. The crystallizer provides a classifying action. Internal circulation keeps growing CN_4 -crystals in suspension till they reach the size convenient for separation. Grain size distribution curve is very narrow, and hence a continually working filtering centrifuge with high specific output and efficiency can be used. In the centrifuge crystals are washed by nitric acid. Apart from the drop of attendance demands and investment costs, CN_4 of high purity with minimum quantity of adhered P_2O_5 is obtained.

1.3 Crystallizer capacity

Due to high intensity of the heat-transfer and high admissible temperature differences the specific output of the crystallizer

is approx. 1.7 ton of P_2O_5/m^3 per day, which exceeds by several times the values required for the classical Odda process. At present crystallizers with daily output of 50 and 75 tons P_2O_5 in mother liquors are in operation. Further increase of the output is under consideration.

1.4 Relative investment costs

Using the direct heat-transfer the installation of the heat-transfer surface in the crystallizers is eliminated. As the circulated heat-transfer medium is pure, the cooling capacity of the external cooler for this medium is so high that the necessary cooling surface decreases substantially to under 50 % of the surface needed for the indirect cooling. High specific output of the crystallizer enables installation of relatively small equipment.

Furthermore the use of efficient centrifuges reduces the relative investments.

The equipment can be placed advantageously into an open, roofed construction.

1.5 Safety

The white spirit hydrocarbon fraction of high boiling range and with flash point over $35^\circ C$ is used as heat-transfer medium. As all operations are performed below the flash point temperatures, the white spirit behaves like a non flammable liquid. In accordance with the regulations, no explosion-proof electric installation is required in these plants. Areas of existing plants where white spirit is worked with are nevertheless equipped with explosion-proof installation so that the increased risk in manufacturing by utilizing white spirit is negligible.

1.6 Raw materials

Acidulation slurry for the crystallization process may be prepared from practically any calcined phosphate rocks. Operating units work with Kola apatite and Morocco phosphate. However, in laboratory and pilot plant several other phosphates such as Florida, Tunisia-Gafsa, Algeria, Jordan, and Spanish Sahara have been tested with the same good results.

Phosphates with high content of aluminium and iron forming non assimilable compounds are less suitable, as in the case of other processes for the manufacture of fertilizers or phosphoric acid. Nitric acid for the attack may have concentration from 50 to 65 %. Optimal concentration is 56 to 58 %. Lower concentration requires lower crystallization temperatures for reaching the same CaO crystallization degree. Higher concentration influences favourably crystallization temperatures, brings, however, an unfavourable influence on the viscosity of the solution and on the proportion of the solid and liquid phase at the crystallizer outlet. These unfavourable influences of concentrated nitric acid can be eliminated by increasing the necessary surplus of the nitric acid from 3.5 up to approx. 10 %.

2. Process description

Acidulation slurry is cooled first by heat exchange with cold mother liquor from the second crystallization step and then by water. The slurry inlet temperature to the crystallizer I lies slightly above the temperature of crystallization.

In the continuous crystallizer I, the slurry is cooled by direct contact with undercooled white spirit to the desired crystallization temperature. The crystals are separated from the internal circulation after reaching an adequate size and gathered in the bottom of the crystallizer. They are continuously discharged together with the mother liquor to the centrifuges where they are separated and washed with nitric acid.

Washed crystals are transported to melting tank and the melt is further pumped to the carboammoniation section.

The heated white spirit overflowing from the top of the crystallizer is recycled via the cooler to the crystallizer. The white spirit is cooled by evaporating ammonia needed for neutralization. Since the refrigerating capacity of this ammonia is usually insufficient to cover the total demand, a certain amount of liquid ammonia from other sources - mostly refrigeration station - is needed.

The mother liquor, collected in mother liquor tank I, is pumped to

the continuous crystallizer II. This crystallizer is usually smaller but in principle of the same type as crystallizer I.

From the bottom the discharged mixture of mother liquor and crystals is separated in centrifuge II. Washed crystals fall to the melting tank mentioned above.

The white spirit from the circulation system of the crystallizer II is cooled by evaporation of ammonia or other refrigerants from a refrigeration station. The same refrigerant is used for cooling nitric acid needed for CN_4 washing. Nitric acid from washing is either returned to the rock acidulation to keep the $\text{N}/\text{P}_2\text{O}_5$ ratio as low as possible or mixed with mother liquor.

The mother liquor from the second crystallization step is collected in tank II and pumped via pre-cooler II and special purification apparatus - not shown on the scheme - into the ammoniation.

3. Quality of products

3.1 Mother liquor and fertilizers

Figure No. 2 shows a typical course of CN_4 crystallization for a solution obtained by the nitric acid attack of Kola apatite.

Curve A shows content of P_2O_5 in mother liquor

B the content of CaO

C the $\text{CaO}/\text{P}_2\text{O}_5$ -ratio and

D shows degree of CaO -crystallization (degree of CaO -separation is a little lower due to the efficiency of the centrifuge)

All curves are drawn as a function of the temperature.

It is evident that in a given case mother liquor with any required content of P_2O_5 up to 30 % (wt) and $\text{CaO}/\text{P}_2\text{O}_5$ -ratio down to 0.15 can be obtained. Mentioned values are obtained with temperatures of approx. -20°C . Further lowering of temperature increases the crystallization degree slightly, while the consumption and cost of frigories go up considerably so that the temperature shown above presents a limiting practicable value.

Figure No 3 shows compositions of fertilizers which can be produced from mother liquors with different degrees of CaO-separation. This table is based on Morocco phosphate, which gives at the same crystallization degree somewhat lower quality of fertilizer both as far as nutrient content and water soluble P_2O_5 -content are concerned, as compared with Kola phosphate, due to higher CaC/ P_2O_5 -ratio.

It shows compositions of fertilizers - so called basic type - when mother liquor is processed without addition of nitrogen and potassium and after their processing into fertilizers 1-1-0 and 1-1-1. An ammoniation degree is assumed corresponding to 10 % of diammonium phosphate and the addition of sludge, separated after the rock acidulation by which the nutrient content is somewhat reduced.

In the last column the theoretical P_2O_5 water solubility is shown after subtracting the P_2O_5 combined with Ca, Al and Fe. But in fact, the P_2O_5 water solubility obtained by analytical control is always higher as Fe and Al are bound to other compounds without or with a lower P_2O_5 content than in ortho salts and as dicalcium phosphate is partially soluble in water in the presence of ammonium nitrate.

The N/ P_2O_5 -ratio is also fixed by the CaO-separation degree.

From the following Figure No 4 the extent of possible N/ P_2O_5 -ratios are evident. The lower curve shows this relation of the basic fertilizer, depending on the separation degree. This curve shows that a N/ P_2O_5 -ratio of 0.5 can be safely obtained. The upper curve gives the N/ P_2O_5 -ratio after recycling the total ammonium nitrate, obtained by converting the calcium nitrate from the separation section, into the fertilizer. The amount of recycled ammonium nitrate as well as additional nitrogen requirements, evidently does not depend on the process but on the desired N-content in the fertilizer. As shown above complex fertilizers of good quality with nutrient content of about 50 % with a P_2O_5 water solubility up to 90 % and with a wide range of N/ P_2O_5 -ratio can be produced by the CHP-SCHZ crystallization process.

A higher P_2O_5 water solubility nearing 100 % can be achieved by eliminating the remaining calcium by adding SO_4 -ions. The thus obtained gypsum can either be left in the slurry or removed from it as has been tested by SCHZ.

By further modification of the process the N/ P_2O_5 -ratio can be reduced down to the value of approx. 0.4.

As the content of white spirit in the fertilizer is so low, it cannot be determined by analysis.

3.2 Calcium nitrate tetrahydrate

Crystallized CN_4 forms well developed grains of the size between 0.35 and 1.2 mm. As the content of the occluded mother liquor after separation is low, the P_2O_5 content does not exceed 0.3 % (wt) in a single-stage and 0.5 % (wt) in a two-stage crystallization.

The content of entrained white spirit is so low that CN_4 can be safely used for producing ammonium nitrate of different concentration without any additional treatment.

4. Utility consumption

The consumption of utilities per ton of P_2O_5 in mother liquor depending on different degrees of separation is shown in Figure No. 5. Values are given for a complete crystallization unit, including CN_4 -separation and melting as well as refrigeration station whereby consumption of gaseous ammonia for mother liquor ammoniation is taken into account.

Curves are based on the utilities requirements for calcined Morocco phosphate (77 BPL) and they depend a little on the type of phosphate and concentration of the acid.

The curve A for the electric power consumption is influenced mostly by the degree of crystallization, as by increasing this, the temperature level decreases at which the frigories have to be available. Ammonia as refrigerating medium has been taken as basis for the power consumption. There is a possible reduction of the power consumption by using other refrigerants, such as freons, for higher crystallization degrees.

Consumption of water - curve B - includes the use of cooling water for acidulation slurry cooling and for the refrigeration station. The increased demand of water for the refrigeration station is most remarkable at high crystallization degrees.

Steam consumption (shown by the curve C) is needed for heating and melting of CN_4 -crystals only.

This figure shows also roughly the range of a single-stage and a two-stage crystallization.

Specific consumption of water and steam for a given degree of crystallization does not depend on capacity. Only specific use of electric power, influenced by the equipment size, is partly dependent on the capacity. This is more evident with low capacities and the consumption expressed in % for capacities 50, 75, 150, 300 mtpd P_2O_5 in mother liquor is for example 100, 88.5, 83.5 and 80.5 for a separation degree of 70 % and 100, 95.5, 93.3 and 92.8 for a separation degree of 88 %.

5. Crystallization process in different fertilizer process routes

5.1 Calcium nitrate tetrahydrate processing

Contrary to the gypsum obtained as inconvenient waste in the wet process phosphoric acid, in the production of crystallization process phosphoric acid - and mother liquors can be taken for that - CN_4 is produced. Its processing complicates the manufacture of fertilizers.

Most natural and economic is its direct processing into calcium nitrate fertilizer. The nitrogen content of 15.5 is low, true enough, but this nitrogen is agrochemically very efficient and in European countries, especially in Scandinavia, this fertilizer is rather popular.

Another suitable alternative is the conversion of CN_4 into ammonium nitrate. This conversion increases considerably the flexibility of the plant as through the processed ammonium nitrate the N/P_2O_5 -ratio of the basic fertilizer can be adjusted as mentioned before. This ammonium nitrate can also be used for the production of calcium ammonium nitrate having 20 - 30 % nitrogen or ammonium nitrate with

33 - 34 % nitrogen, which is exceptionally favourable for companies producing this type of fertilizer anyway.

A certain part of ammonium nitrate can be sold for other technical purposes. For countries, preferring liquid fertilizers, it is easy to prepare nitrogen solutions containing 30 - 40 % of N, both from ammonium nitrate as well as from calcium nitrate, by means of a simple equipment. Another comparatively suitable application is the production of nitrate urea made by mixing CN_4 and urea in different molar proportions. For example with molar proportion 1 : 1 a fertilizer with 21.2 % N, with molar proportion 1 : 4 a fertilizer with 32 % N can be obtained.

Thermal decomposition of calcium nitrate for recovery of nitric acid is still in the development stage.

5.2 Crystallization process phosphoric acid - treatment

Both operation units that have been realised work with the so-called classical granulation, i.e. with granulation in pugmills followed by drying and cooling in rotary drums. This process enables a greater flexibility and adaptability as far as the quality of the fertilizer is concerned.

But it should be pointed out that the incorporation of the crystallization unit is not restricted to a special technology for processing of mother liquor or of CN_4 . As the requirements of the agriculture and fertilizer industry are manifold, there is not any universal technology which meets all these. For this reason a prilling technology has been developed by SCHZ Lovosice which enables to process most of the nitrophosphate fertilizer down to a $\text{N/P}_2\text{O}_5$ -ratio of 0.6.

Furthermore the processing of the crude phosphoric acid into a high concentrated product equivalent to super phosphoric acid is in the final development stage. This technology is very interesting especially for the production of liquid fertilizers and phosphorus compounds for technical use. But also other proven technologies can be utilized for processing the mother liquor - e.g. prilling, melt granulation, spray granulation by spherodisers, fluid-bed granulation and flaking.

III. BAMAG CHEMOPROJEKT NITROPHOSPHATE PROCESS

1. Combination of industrialized process steps

After having outlined the features of the new continuous crystallization process by direct heat transfer the second part of this paper deals with a new complete NPK-process basically consisting of a combination of commercial size proven process steps. The new BAMAG CHEMOPROJEKT PROCESS starts with the nitric acid attack of phosphate rock and the direct CN_4 -crystallization according to the know-how from Severoceske Chemicke Zavody, Lovosice / CSSR and uses the granulation and carboammoniation know-how from Chemische Fabrik Kalk, Cologne/Germany. The first plant according to this combined know-how was successfully started this year.

2. First Plant according to the BAMAG CHEMOPROJEKT PROCESS

2.1 Design Data

The first commercial size plant according to the BAMAG CHEMOPROJEKT PROCESS has a design capacity of 60 mtpd P_2O_5 in the NPK-product. Based on this P_2O_5 -capacity the following NPK-formulas with their respective throughputs are produced:

12 - 24 - 12: capacity 250 mtpd
16 - 16 - 16: capacity 375 mtpd
12 - 12 - 24: capacity 500 mtpd.

The feedstocks being

Morocco phosphate, calcined 77/79 BPL
Nitric acid 56 % (wt)
Ammonia liquid
Potassium chloride (60 % K_2O)
Carbondioxide.

As the required minimum P_2O_5 -water-solubility of all the three NPK-products is 80 %, the degree of separation of CaO from the phosphate rock has to be as high as 88 %. This is realized by a two-step crystallization. This high CaO-separation results in the production of a fertilizer having a $\text{N}/\text{P}_2\text{O}_5$ -ratio of 0.5 without using additional phosphoric acid as feedstock. It is of course possible to produce different NPK-formulas, too, having a $\text{N}/\text{P}_2\text{O}_5$ -ratio between approx. 0.5 and 2.0 without use of additional nitrogen.

Due to the high P_2O_5 -water-solubility of these fertilizers, such nitrophosphate plant is only comparable with a combination of a phosphoric acid plant and a classical fertilizer plant. But due to the production of precipitated calcium carbonate and concentrated ammonium nitrate solution as valuable by-products all problems with removal or use of byproduct gypsum are eliminated.

2.2 Process description

According to the figure No. 6 the whole plant can be divided into the following main parts:

1. Rock phosphate acidulation and crystallization
2. NPK-production by ammoniation, granulation, drying and conditioning
3. Carboammoniation, calcium carbonate filtration and ammonium nitrate concentration.

The following process description refers to the above mentioned parts of the plant.

Acidulation and crystallization (Figure No. 7)

The phosphate rock is fed to acidulation vessels (1) where it is decomposed with a slight excess of nitric acid under suitable temperature and stirring conditions ensuring the most efficient attack.

A part of the required nitric acid serves for washing of the CN^4 -crystals and is therefore passed via acid cooler (22) and centrifuges (11), (17) into the rock acidulation. Fluorine compounds and nitrous gases formed during acid attack are scrubbed with water - circulated in column (3) by pump (4) - and exhausted by fan (5). To ensure a smooth crystallization the acidulation slurry is separated from insolubles in decanter centrifuge (3).

The clarified slurry is pumped by (6) to refrigeration recovery cooler (7) where it is cooled by the chilled mother liquor and further cooled down in (8) before fed into the first crystallizer (9).

Since a detailed description of the crystallization process has al-

ready been given in part I of the paper, it should only be mentioned here that the frigories for the first crystallizer are supplied by evaporation of the ammonia used in the process. Since these frigories do not cover the requirement, the remaining demand is supplied by a white spirit stream from the second crystallization step bypassing the second crystallizer. The second crystallizer is connected to the refrigeration plant.

The suspensions of CN_4 -crystals in the mother liquor originating from the crystallizers (9, 15) are separated and the obtained crystals washed with cooled nitric acid in centrifuges (10, 16).

The used acid is sent into the rock acidulation and the CN_4 -crystals are fed to the melting vessel of the carbo-ammoniation section. After admixture of the sludge from centrifuge (3), the mother liquor is pumped by (21) to the fertilizer production section.

Neutralization, Granulation and Conditioning (Figure No. 8)

The mother liquor is adjusted with ammonium nitrate according to the required $\text{N}/\text{P}_2\text{O}_5$ -ratio and neutralized with gaseous ammonia under intensive agitation in vessel (25). Thereby part of the water vaporizes.

The ammoniated slurry is further concentrated, to obtain the best conditions for granulation, in forced-circulation evaporator (27, 28). The vapours are exhausted by fan (29). According to the desired formula potassium chloride is added in vessel (30). The obtained slurry with the required nutrient content is granulated with dried recycle from hopper (38) in pug-mill (32). Liquid ammonia is added to support the granulation as well as to adjust the final pH-value of the product. The ammoniation vessel, potassium adding vessel and granulator are exhausted by fan (31).

The final nutrient concentration is adjusted by ballast from hopper (40). The product is dried in flue gas heated drum (33). The waste gas is separated from dust in cyclones (47) and exhausted by fan (48). The dried product is elevated by (34) and separated into oversize undersize and product size by screen (35). The oversize and part of the product size are crushed by (36 and 37) and together with the undersize and the dust from the cyclones collected in hopper (38).

Hopper (38) controls the recycle feed independent of the just produced undersize and oversize.

The near mesh material is eliminated from the product grain at screen (41).

To improve the storage stability, the product is cooled in fluid-bed cooler (42) by air drawn in from fan (44) and conditioned in heat exchanger (43). The air is separated from dust in cyclones (49) and exhausted by fan (50). The NPK-granules are coated with kieselguhr from hopper (45) in drum (46).

CN4-Processing (Fig. 9)

The CN4-crystals are melted with steam in vessel (51). The obtained solution is converted into calcium carbonate and ammonium nitrate under addition of carbon dioxide and ammonia in reactor (52). The heat of reaction is removed with cooling water.

The waste-gas from the reactor is exhausted by fan (56) after scrubbing with nitric acid in tower (53) to reduce the ammonia losses. The wash acid is circulated by pump (54) via cooler (55). This wash acid serves simultaneously for neutralization of the ammonium nitrate solution in vessel (68).

Calcium carbonate is separated from the ammonium nitrate solution and washed in drum filter (57), then dried in the flue gas heated pneumatic dryer (70) and separated in cyclone (71) and bag filter (72). The drying air is exhausted by fan (68).

The ammonia nitrate solution is neutralized in vessel (58), delivered by pump (59) to a 4-stage concentration unit consisting of circulation pumps (61), exchangers (60), evaporators (62), condensers (63) and vacuum pump (64), where the solution is concentrated up to 95 % before sent to battery limits.

3.3 Special features of the BAMAG CHEMOPROJEKT PROCESS

The use and combination of commercial size proven process steps with individual advantages from the commercial and technical point of view results in a process which offers a high technical reliability at comparable investment and production cost. Usually, the design of an individual plant requires a precise incorporation of the fle-

xibility with respect to the production of different formulas or qualities - especially P_2O_5 solubility - which in this case is possible with only minor modifications in the equipment, practically not affecting the overall investment cost. The individual advantages of the main process steps can be summarized as follows:

Under suitable stirring conditions in the rock acidulation the residence time distribution is narrow enough to ensure at least 99.5 percent efficiency at low nitric acid surplus and nitric acid loss, minimizing the equipment expenditure.

The advantages of the continuous direct cooled crystallization have already been outlined in detail in the first part of the paper.

The low degree of ammoniation of the mother liquor decreases the reformation of waterinsoluble P_2O_5 -components.

According to the overall water balance, in many cases a concentration step for the ammoniated slurry is recommended since the concentration of the nitric acid feedstock is limited for different reasons, e.g. acidulation conditions, viscosity of the mother liquor in the crystallization step, required minimum nitric acid surplus for N/P_2O_5 -ratios at the low limit.

In any case, this concentration step will increase the reliability of the granulation and, above all, the flexibility of the whole process with respect to the processing of different phosphate rocks and to the variation of the degree of crystallization which in turn accounts for different water solubilities, nutrient concentrations and N/P_2O_5 -ratios.

At low investment costs a pugmill offers safe and stable granulation conditions which results in a low recycle ratio. A buffer in the recycle loop ensures an exact control of the recycle absolutely independent of the just produced undersize and oversize. This combination in the granulation loop increases the flexibility and, moreover, the reliability during extreme operating conditions.

The use of a special reactor for the carboammoniation of the CN_4 has been well proven on a commercial scale for over ten years which

is a guarantee for the reliability of this process step. The filtrability of the precipitated calcium carbonate is such that the suspension is separated without any difficulty.

By reprocessing of the obtained byproduct ammonium nitrate into the NP-slurry, it is possible to produce fertilizer with a N/P_2O_5 -ratio from 0.5 to approx. 2.0 without additional use of nitrogen.

3.4 Economies

Figure No. 10 sums up the raw material and utilities consumptions for the above described plant considering the three different NPK-formulas. The expected overall efficiencies are as follows:

P_2O_5 (available)	96 %
N - total	97 %
K_2O	99.5 %

It can be seen from this table that in order to reach the exact formulas it is necessary to add some ballast into the product. This is even necessary for the 16-16-16 product, since the CaO-separation degree includes a certain safety margin in order to reach the required percentage of water-soluble P_2O_5 -content in the NPK-product.

Figure No. 10 gives the production costs for the three products based on average West-European conditions.

The following assumptions have been made:

Carbon dioxide is available at no cost, for instance from an existing ammonia synthesis unit.

The credit for the 95 % conc. ammonium nitrate solution is based on the cost for the production by direct neutralisation of nitric acid with ammonia and is taken as raw materials costs, adding 35 % for utilities, labour, maintenance, capital return etc.

Labour costs include 50 % overhead but varies considerably depending on the skill-levels of the operators and the degree of automation of the plant. Fixed costs are based on a total turn-key investment of 21.3 Mio DM, a depreciation rate of 10 % per year, an interest rate of 5 % per year and maintenance costs (incl. spare parts)

of 2 % per year which is approx. 3 % of the investment for the equipment. It should, of course, be mentioned that for individual cases the figures of this table can vary considerably for different unit costs of raw material and utilities, different labour costs and different basis for equipment prices. For instance it is known that even in different West-European countries the investment costs deviate. Hence these figures give only an overall picture of the economies.

To summarize one can say that for the given plant size approx. 75 % of the production cost are due to raw materials and utilities, approx. 20 % are due to capital costs and only approx. 5 % are due to cost for labour and maintenance. This approx. 20 % part of the total production costs for capital demonstrates that the plant is at the lower limit of an economical size.

The next figure No. 12 illustrates at first the tendency of the production costs at different plant capacities on the same basis as for the above mentioned calculations. It has to be mentioned that the production costs of the above described plant do not exactly fit into this diagram, since this plant is designed according to the requirements of the production of 500 mtpd of the formula 12-12-24. This means basically that granulation, drying and finishing equipment is capable to handle 500 mtpd fertilizer instead of 375 mtpd if only formulas of the type 1-1-1 have to be produced.

One can see that there is for instance for the 16-16-16 product only a decrease in the production costs of approx. DM 12.-- per ton of NPK or 10 %, if the capacity increases from 500 to 1,000 mtpd. The same tendency is valid for the other formulas as shown in the diagram.

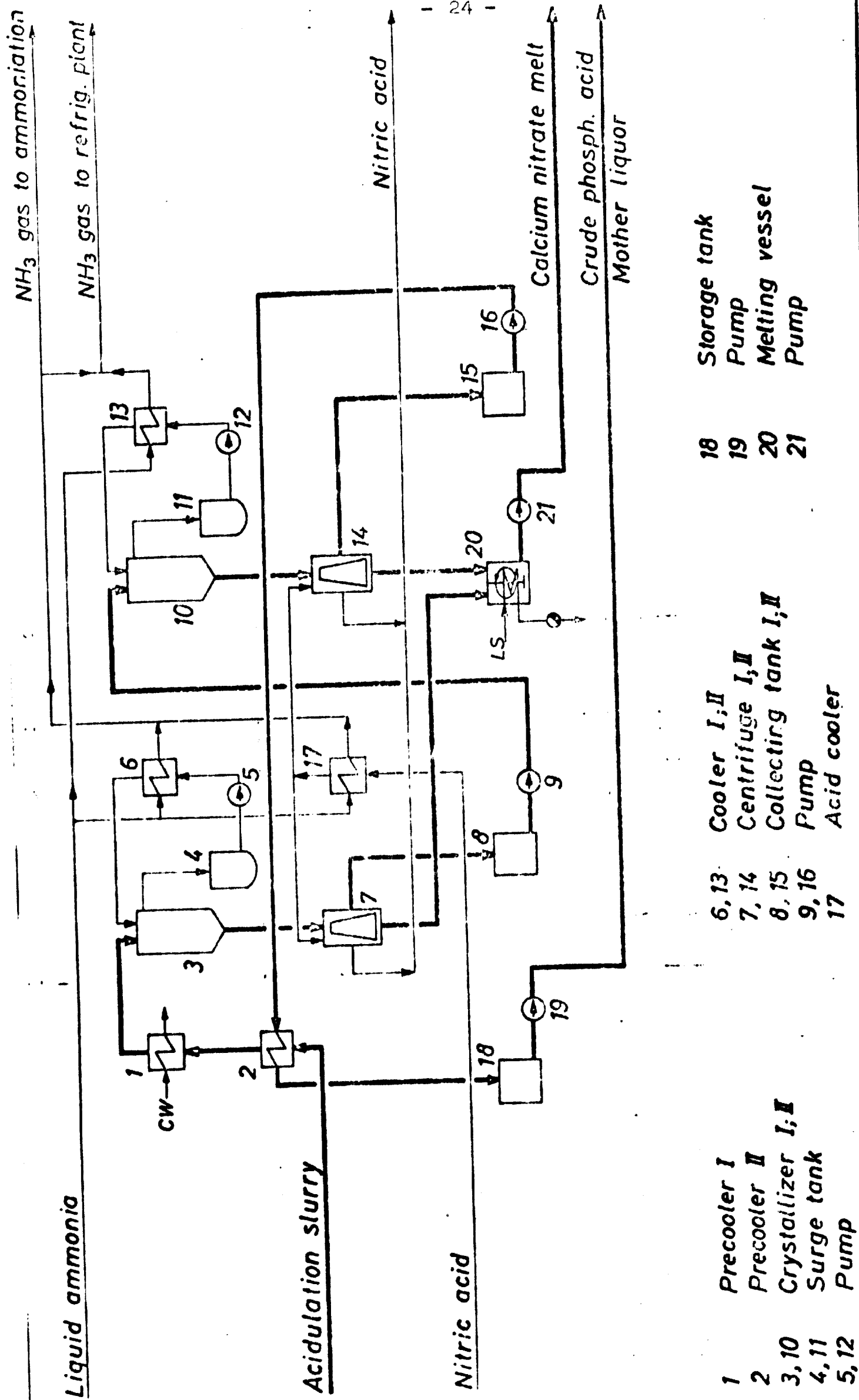
Furthermore the production costs are calculated for different nutrient concentration in fertilizers of type 1-1-1 in order to demonstrate the economy of different degrees of crystallization.

The production costs for 17-17-17 are of course higher than for 15-15-15. The difference is caused by two reasons: At first the

higher nutrient content per ton NPK of 17-17-17, secondly the higher investment and utility costs for a plant to produce NPK-formulas of higher nutrient content. The first part can be compensated by adding the additional raw material costs according to the higher nutrient content per ton of NPK. The dotted lines give this compensation both recalculated on the basis of 17-17-17. The remaining difference to the actual curve of the 17-17-17 product represents the higher investment and utility consumption according to the larger crystallization step and carboammoniation unit, since an increased nutrient concentration corresponds only to a higher degree of CaO-separation.

This means for the production of considerably more valuable products the necessary higher overall investment is very small and therefore is reflected in the cost of one ton of NPK by a very small percentage. In other words, a very small increase of the overall investment costs enables a high flexibility of the plant with respect to different NPK-formulas and - from the economical point of view - a very attractive possibility of the production of highly valuable NPK-products. The small additional production costs for more valuable products are not comparable with the difference of the market price for NPK-fertilizers having lower or higher total nutrient contents.

A comparison of the production of high water-soluble NPK-fertilizers between nitrophosphate and phosphoric acid route has been dispensed with, since enough information is available in the literature.



- | | | | |
|-------|-----------------------|----|----------------|
| 1 | Precooler I | 18 | Storage tank |
| 2 | Precooler II | 19 | Pump |
| 3, 10 | Crystallizer I; II | 20 | Melting vessel |
| 4, 11 | Surge tank | 21 | Pump |
| 5, 12 | Pump | | |
| 6, 13 | Cooler I; II | | |
| 7, 14 | Centrifuge I; II | | |
| 8, 15 | Collecting tank I; II | | |
| 9, 16 | Pump | | |
| 17 | Acid cooler | | |

Figure 1

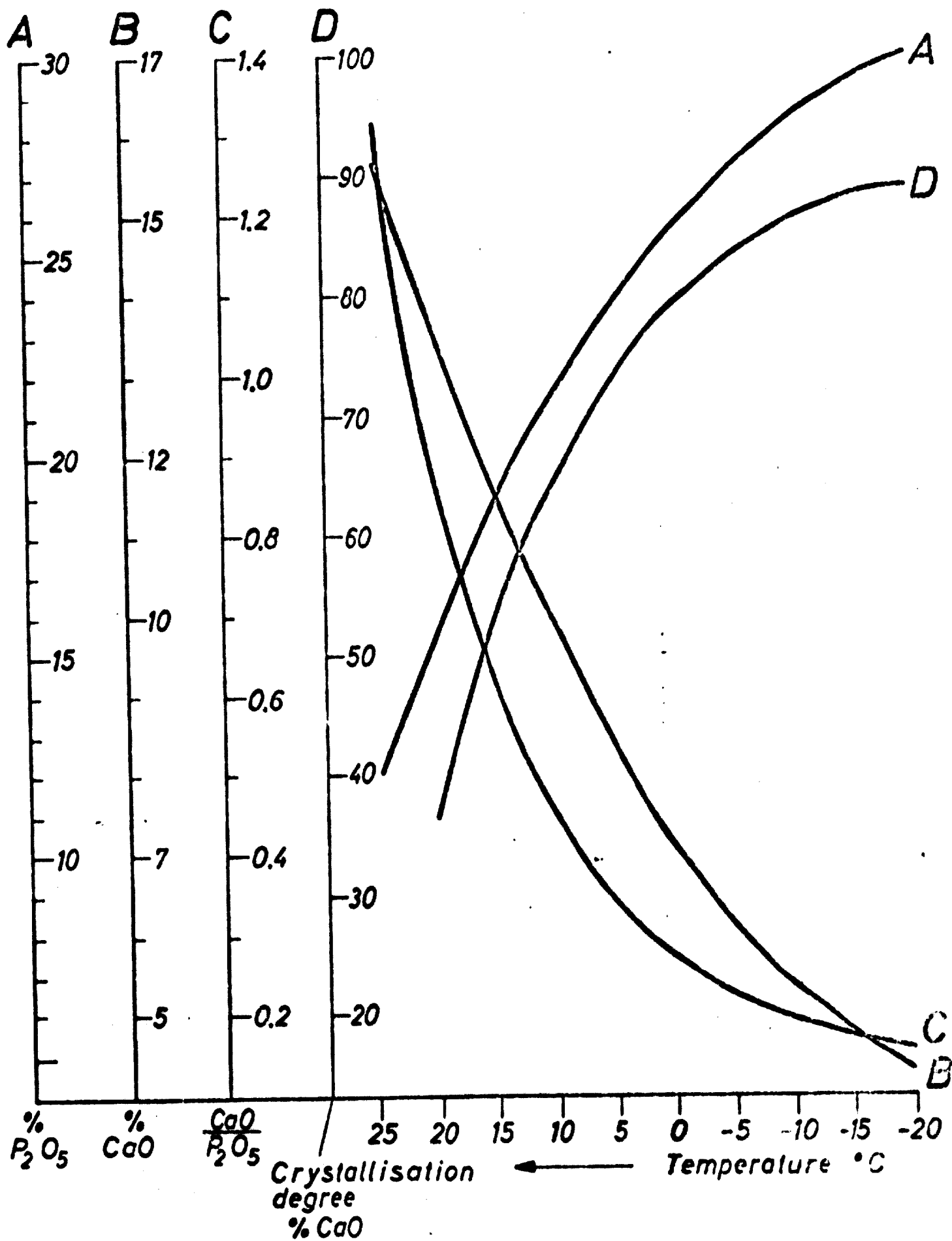


Figure 2

Typical Crystallization Course

Ca Separation Degree	N : P ₂ O ₅ : K ₂ O			Water Soluble P ₂ O ₅ % (min)
	Basic Type	1 - 1 - 0	1 - 1 - 1	
%				
56	18.6 - 22.4 - 0	20.2 - 20.2 - 0	15.1 - 15.1 - 15.1	27
70	17.9 - 26.6 - 0	21.3 - 21.3 - 0	15.7 - 15.7 - 15.7	53
80	17.3 - 30.6 - 0	22.1 - 22.1 - 0	16.1 - 16.1 - 16.1	72
85	16.9 - 33.2 - 0	22.5 - 22.5 - 0	16.3 - 16.3 - 16.3	81
88	16.6 - 34.9 - 0	22.8 - 22.8 - 0	16.5 - 16.5 - 16.5	87

Figure 3
Product Quality

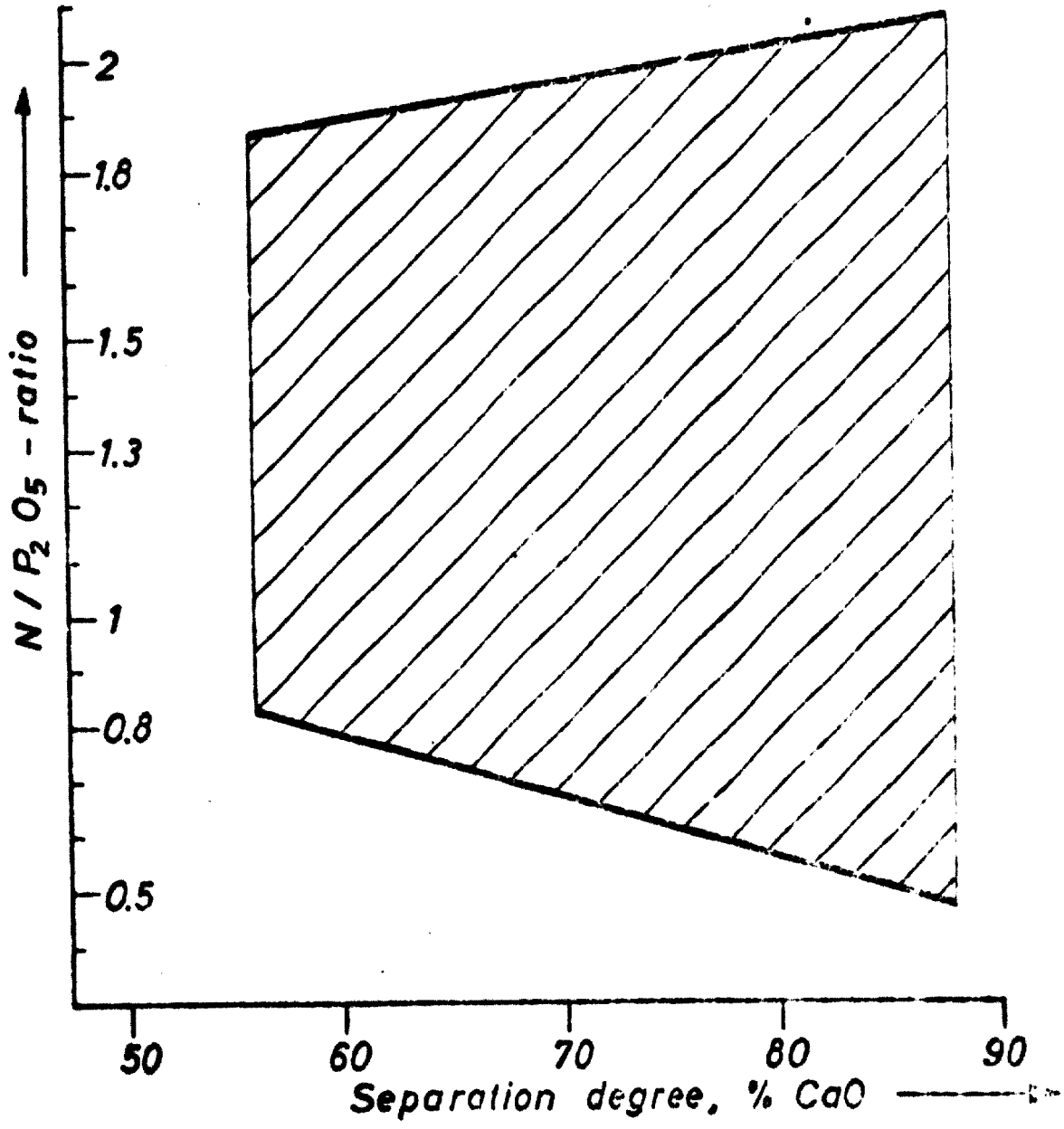


Figure 4

N / P₂ O₅ - ratio in the Fertilizer

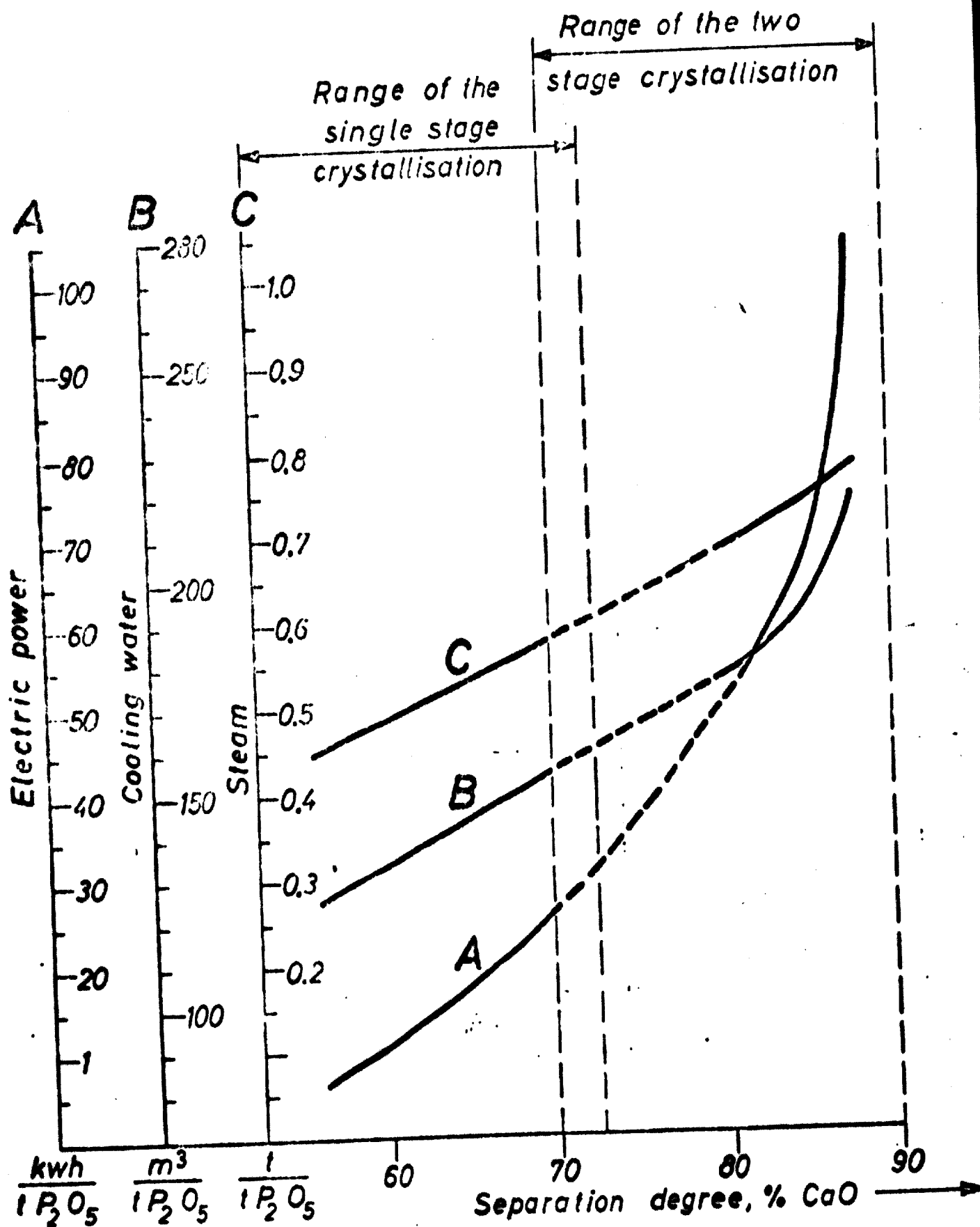


Figure 5

Specific Utility Consumption
of the Crystallisation

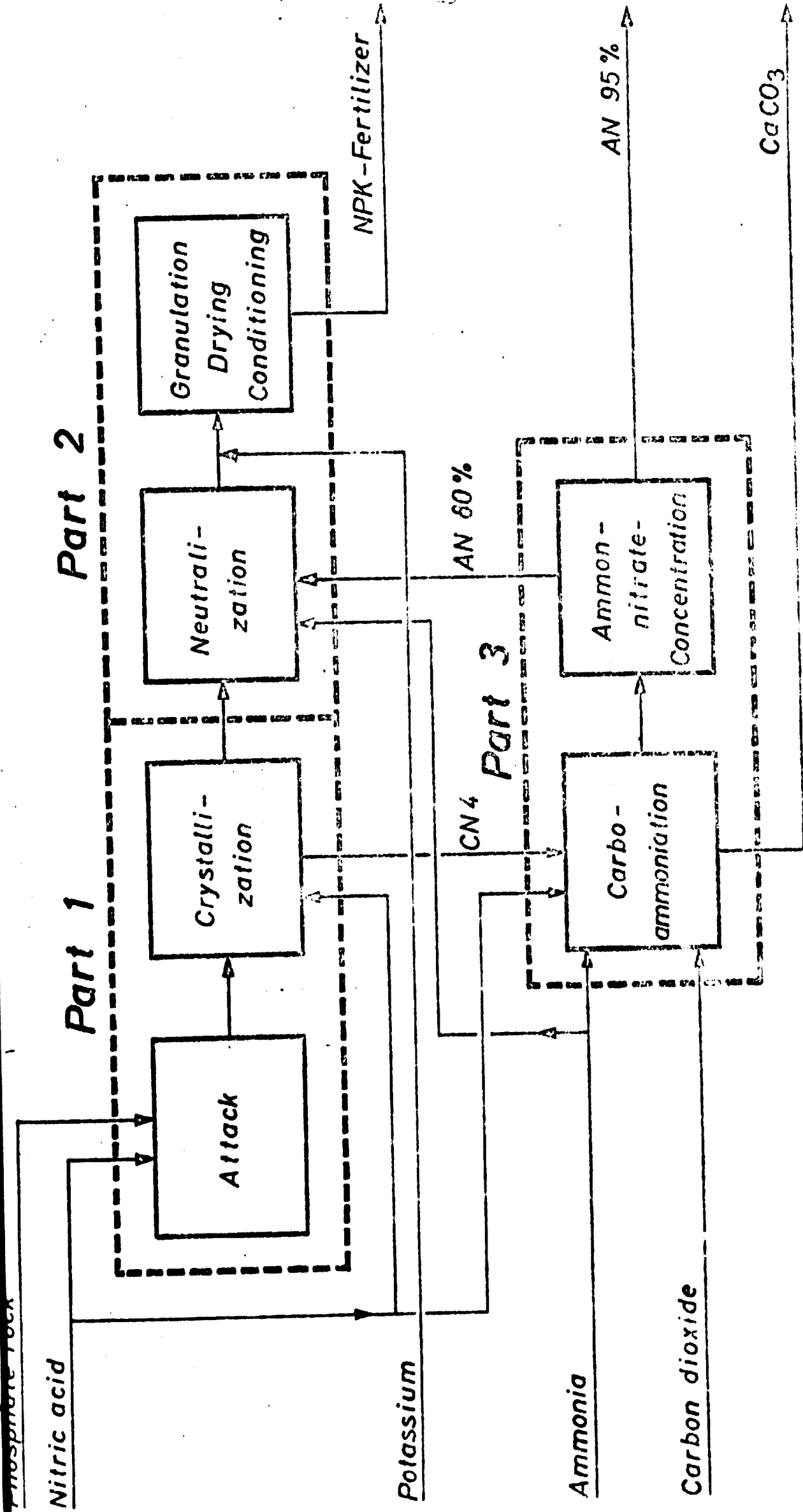
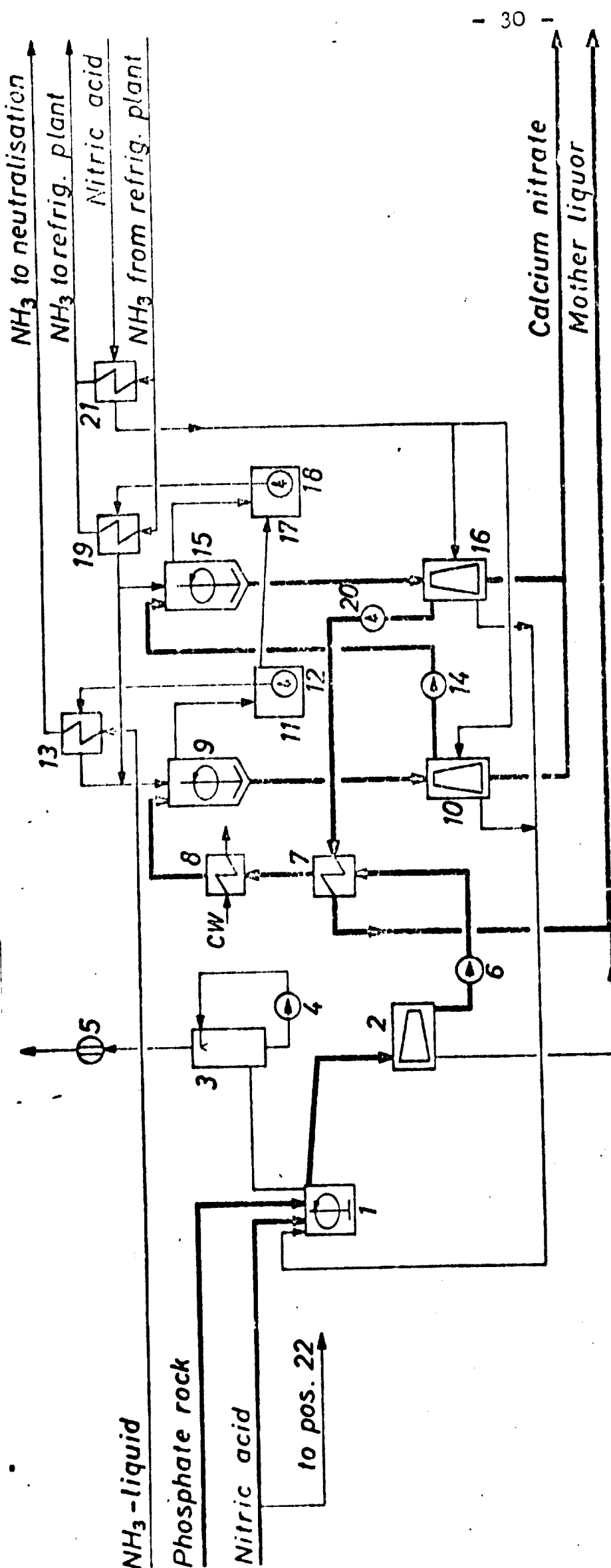


Figure 6

Block Diagram of the Nitrophosphate Plant

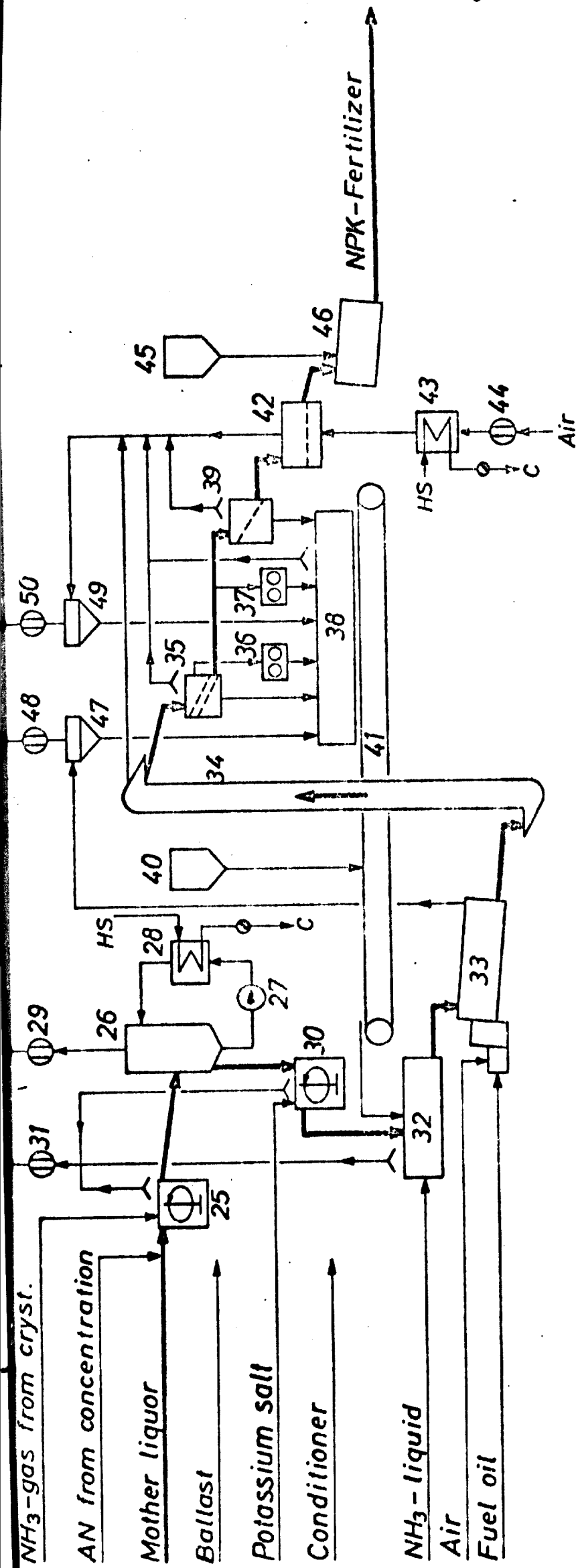


14, 20 Mother liquor pump
21 Acid cooler

7, 8 Precooler
9, 15 Crystallizer
10, 16 Centrifuge
11, 17 Surge tank
12, 18 Pump
13, 19 Cooler

1 Acidulation vessels
2 Decanter centrifuge
3 Wash tower
4 Pump
5 Fan
6 Slurry pump

Figure 7
Flowsheet of the Attack and Continuous Crystallisation

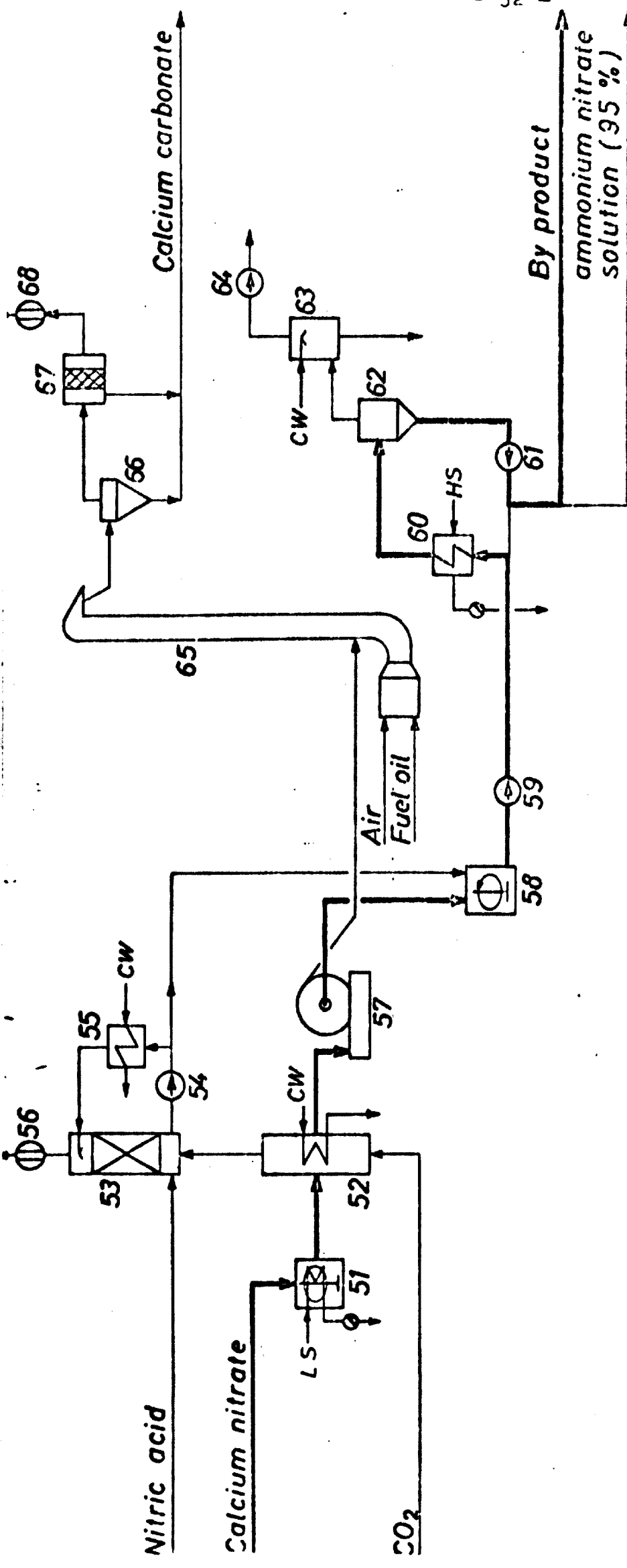


- 25 Ammoniation vessel
- 26 Evaporator
- 27 Circulation pump
- 28 Heat exchanger
- 29, 31 Fan
- 30 Mixing vessel
- 32 Pugmill
- 33 Drying drum

- 34 Elevator
- 35 Screen
- 36 Ring crusher
- 37 Roller crusher
- 38 Buffer hopper
- 39 Screen
- 40 Ballast hopper
- 41 Belt conveyor

- 42 Fluidized bed cooler
- 43 Air heater
- 44 Blower
- 45 Coating powder hopper
- 46 Coating drum
- 47, 49 Cyclones
- 48, 50 Fan

Figure 8
 Flowsheet of the Fertilizer Production Unit
 Part 2



- | | | | |
|----|-----------------------|----|-----------------|
| 51 | Melting vessel | 63 | Condenser |
| 52 | Reactor | 64 | Vacuum pump |
| 53 | Wash tower | 65 | Pneumatic dryer |
| 54 | Pump | 66 | Cyclone |
| 55 | Cooler | 67 | Bag filter |
| 56 | Fan | 68 | Fan |
| 57 | Drum filter | | |
| 58 | Neutralization vessel | | |
| 59 | AN-pump | | |
| 60 | Heat exchanger | | |
| 61 | Circulation pump | | |
| 62 | Evaporator | | |

Figure 9
 Flowsheet of Carboammoniation with CaCO_3 -Drying and AN-Concentration

Formula	12-24-12	16-16-16	12-12-24
Production figures per hours			
NPK fertilizer kg/h	10 370	15 560	20 750
Ammon nitrate solution (95% conc.) kg N/h	3 710	2 465	2 465
CaCO ₃ kg CaCO ₃ /h	6 140	6 140	6 140
Consumption figures per mt NPK-fertilizer			
<u>Raw materials</u>			
Marocco phos.77/79 BPL kg P ₂ O ₅	249.8	166.5	124.8
Nitric acid kg N/NO ₃	224.7	149.8	112.3
Ammonia kg N/NH ₃	267.9	178.5	133.8
Potassium chloride kg K ₂ O	120.5	160.7	241.0
Carbon dioxide kg CO ₂	298.9	199.4	149.5
Conditioner kg	10	10	10
Ballast kg	38.6	6.5	29
Water m ³	2.1	1.4	1.1
<u>Utilities</u>			
Steam kg	899	609	456
Fuel oil kg	31.3	24.8	19.05
Electricity kwh	149.5	103	77
Cooling water m ³	55	36.7	27.5
White spirit kg	2.42	1.61	1.205

Figure 10
Production and Consumption Figures

Turn key price		21.3 Mio DM			
Formula		12-24-12	16-16-16	12-12-24	
Capacity mtpd		250	375	500	
	Unit	Price DM/unit	Cost DM/mt		
Marocco, calcined 77/79 BPL	mt	63.--	43.97	29.30	21.99
Nitric acid	mt	59.--	59.65	39.65	29.80
Ammonia	mt	130.--	42.38	28.21	21.19
Potassium chloride	mt	120.--	24.12	32.16	48.24
Kiesel guhr	mt	85.--	0.85	0.85	0.85
Power	Kwh	0.05	7.50	5.15	3.85
Cooling water	m ³	0.05	2.20	1.48	1.10
Process water	m ³	0.10	0.21	0.14	0.11
Steam, saturated	mt	5.--	4.50	3.05	2.28
Fuel oil	mt	150.--	4.65	3.75	2.85
White spirit	mt	240.--	0.58	0.38	0.29
Condensate credit	mt	1.30	- 1.13	- 0.75	- 0.57
Ammon nitrate 95% credit	mt	104.--	-113.25	-50.13	-37.55
Operating costs			76.23	94.24	94.33
Maintenance, spare parts	%	2	5.16	3.44	2.58
Labour (+ 50% overhead)	year	700,000.--	8.72	5.81	4.36
Depriciation	%	10	25.82	17.21	12.41
Interest	%	5	12.91	8.61	6.46
			128.84	129.31	120.64

Figure 11
Production Costs

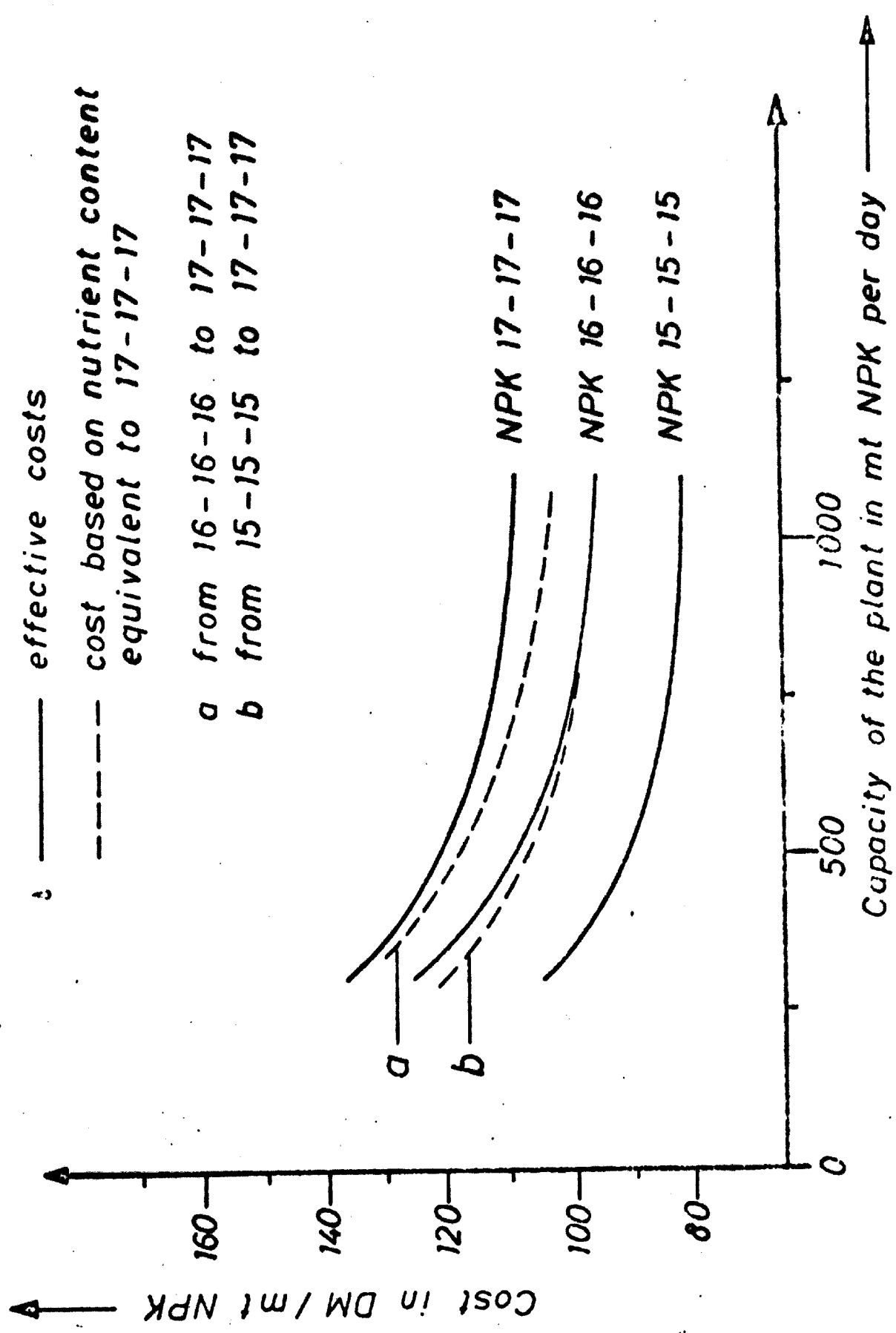
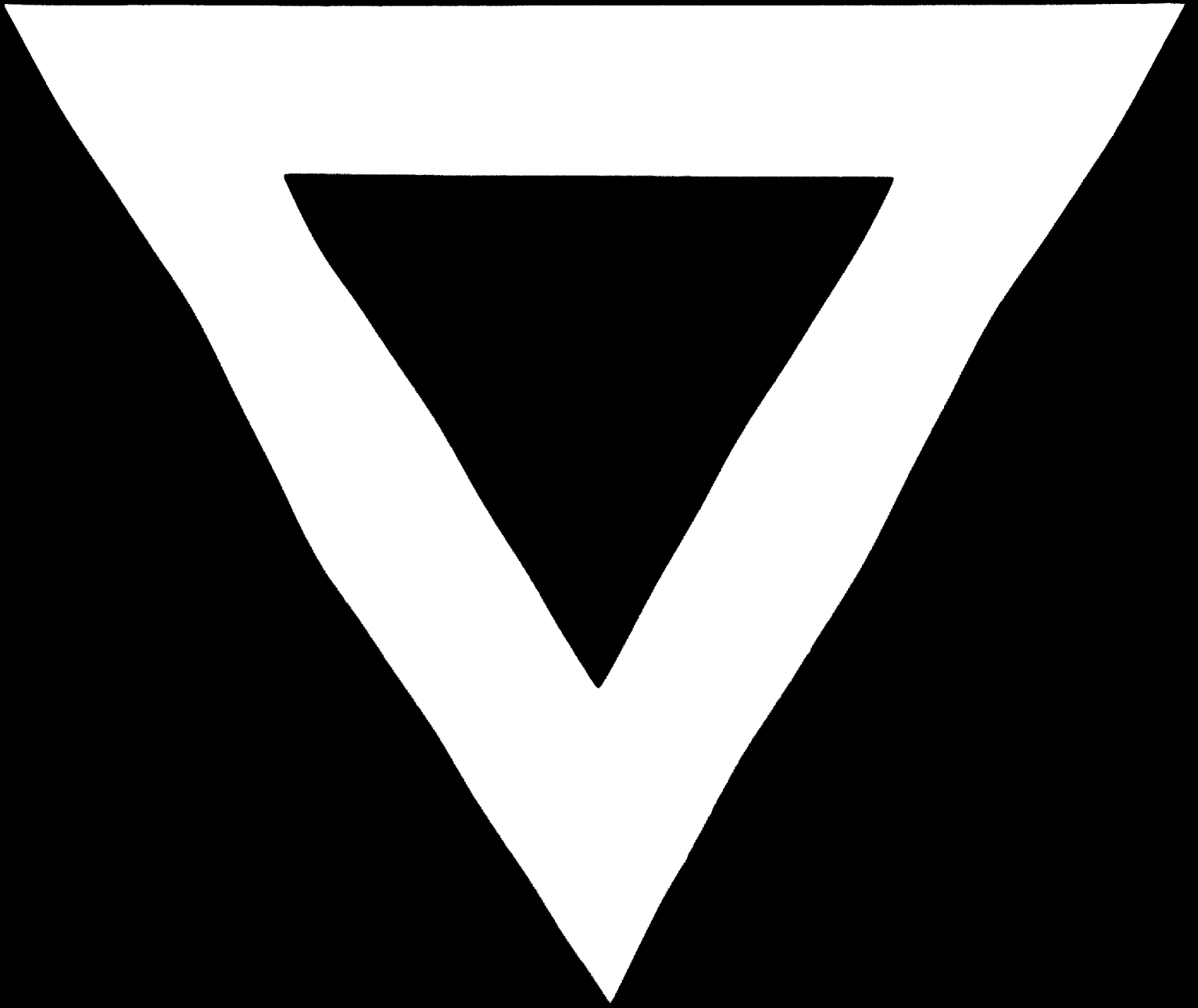


Figure 12
Production Costs
Depending on the Capacity



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