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BUREAU D'ETUDES
INDUSTRIELLES ET
DE COOPERATION DE
L'INSTITUT FRANCAIS
DU PETROLE

PETROVIETNAM
PRE-INVESTMENT STUDY

VOLUME 4
FERTILIZERS

B/F FERTILIZERS

C/F VIETNAM

P. 124

DEI.78060.

December 1978
Ref. 31380.A

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1. FERTILIZERS - GENERAL AND INDUSTRIES

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1. FERTILIZERS - GENERAL

1.1. EFFECT OF DIFFERENT FERTILIZERS ON PLANTS

1. CLASSIFICATION

Fertilizers may be divided into three categories :

- Fertilizers as such, or major elements : these are nitrogen (calculated as N), phosphorus (calculated as P_2O_5) and potash (calculated as K_2O).

- Ameliorators : these include lime, magnesia, plaster, humus, clay and sand, and are used to improve the physical, chemical and biological properties of the soil in order to enhance the effect of the fertilizers themselves.

- Micronutrients, or minor elements, boron, manganese, zinc, nickel, etc... These are found in trace form only, but are nevertheless vital to plant growth, both in quantity and in quality. A lack -or an excess- of these elements is particularly noticeable.

2. FARMING PRACTICES

To allow a seed to breathe and develop into a plant with good roots and radicles, the earth has to be broken up. Plant growth requires substantial amounts of water which can be retained only if the earth is able to absorb rain water.

The aim of the various farming operations practices -ploughing, harrowing, rolling, hoeing- is to break up the earth suitably, but these alone are not sufficient to achieve the optimum physical condition ; the tilth has to be corrected by the addition, often in considerable quantity, of whatever constituent is lacking, e.g. humus, clay, lime or sand. This is the prime purpose of ameliorators.

The microbial life of the soil, a great stimulant to plant growth, has to be encouraged : enemies such as infusoria and protozoa can be combatted by special applications, e.g. carbon disulphide, lime hypochlorite, but most important is to promote microbial development by creating a favourable environment : this is the second purpose of ameliorators.

3. AMELIORATORS

1. Humus

Humus results from lignin decomposition. It is introduced into soil in the shape of natural or artificial manure and organic matter such as leaves which rot giving leaf mould, brushwood, rush, branches, manure crop, etc..

Humus lightens the soil and holds water. It favours bacterial growth.

The liquid manure found in farm manure contains 1 to 2 million bacteria per gram.

It plays a part in plant feeding in the form of calcium humate and also acts to solubilize and disperse P_2O_5.

The fact that it forms humic acids which neutralise with lime points to its tendency to acidify soils.

2. Lime

Lime must be added regularly to soil to neutralise the action of humic acids.

Lime plays an important part in nutrition.

It breaks up soils that are over-solid, i.e. those with high a clay content.

For liming either quicklime, left in little heaps in the fields to burn out before being spread over the earth, or else crushed slaked lime, which can be applied at once, is used.

3. Limestone

Powdered limestone is used, the finer the harder (60/100/180 riddle). Its effect is to release potash by ion transfer from insoluble compounds.

4. Plaster

Plaster also has the property of causing clay to coagulate, thereby lessening the impermeability of the soil. It helps form absorbent complexes, and encourages nitrification (pH).

5. Clay, Sand

In some cases too light soils have to be corrected by the addition of fertilizers to the tilth. Conversely, over-heavy soils can be improved by having sand added.

4. ELEMENTS AND FERTILIZERS

1. Carbon

Carbon derives from carbon dioxide (air, water). The gas is broken down by leaves under the effect of sunlight, the carbon being fixed and the oxvgen given off into the atmosphere - this is the chlorophyllian respiration.

Lighting has an important effect on chlorophyllian assimilation and synthesis. Lighting covers not only visible light but also infra red and ultra violet - maximum photosynthesis energy occurs at around 6550 A.

2. Oxygen

Oxygen derives from water and carbon dioxide.

3. Hydrogen

Hydrogen is obtained from water.

All these elements (C, H_2, O_2) would combine in the form of carbohydrates which through polymerisation would yield glucose which in turn by giving off water and oxygen would generate cellulose.

4. Nitrogen

Function

Nitrogen is the essential vital element, as it goes to make up protoplasm, albumin, and above all protein and chlorophyl. It generally determines growth. It is found in the highest concentrations in young tissue.

In addition nitrogen feeds the micro-organisms in the soil, promoting decomposition of organic matter.

Sources

Nitrogen is obtained from three sources :

a) The atmosphere

Some bacteria fix atmospheric nitrogen directly whereas others change nitrogenous matter into nitric ions. Plants that fix nitrogen are generally of the leguminous type.

b) Vegetable decomposition and organic matters

Decomposing vegetables (manure, oil cake of various sorts) and organic matter (blood, horn, hair, skin, etc..) constitute sources of organic nitrogen and follow the nitrogenous matter transformation cycle.

c) Fertilizers

Fertilizers provide nitrogen in two forms :

Ammoniacal form : phosphate of ammonia, ammonium sulphate, not always absorbed immediately by plants as bacterial action is first required to change them into nitric nitrogen.

Note the direct application of ammonia as a fertilizer. It can be added directly to the soil in the form of either water solution or liquid anhydrous ammonia. Unlike nitric nitrogen, this type of ammonia remains in the ground and is not washed away by rain water. Nitrification speed depends on the acidity of the soil.

Nitric form : sodium nitrate, lime nitrate, potassium nitrate, ammonium nitrate - these fertilizers can be assimilated immediately by plants, and their effect is very strong.

In nitrate form, nitrogen is soluble ; it encourages plant stem and leaf growth but does not increase the plant's resistance. Plants cannot get rid of surplus nitrogen, since it stimulates leaf growth. At the same time it also enhances evaporation, thus in a hot climate a surplus of nitric nitrogen is particularly dangerous.

5. *Phosphorous*

- Function

Phosphorous plays a major part in cell composition (phytin, lecithin) and in forming fats and fruits.

It determines crop quality, regulates growth and lessens the risk of crops being beaten down. It is vital to bone formation, and together with nitrogen governs growth.

- Sources

It is customary in agriculture to consider phosphoric units, not in the phosphorous form (P) but in the form (P_2O_5) ; thus when fertilizer strength is referred to in terms of phosphoric acid, e.g. a super 15 %, such as fertilizer then contains 15 % P_2O_5, not 15 % P.

a) Farm manure

Manure always contains a certain amount of phosphorus. In addition, the organic content has a beneficial effect on the soil, breaking it up and allowing some of the minerals in the soil to be assimilated.

b) Ameliorators and fertilizers

- Ground phosphate : this is a low-solubility ameliorator, lasting 4 to 5 years.
- Basic slag, which always contains free lime - especially suitable for acid soils.
- 40 % P_2O_5 bicalcic phosphates, which though non water-soluble can be totally assimilated.
- Superphosphates of 14/16/18/20 % strength where phosphorus in the form of mono-calcareous phosphate is mostly water-soluble.
- Salts, such as ammonium phosphate, nitrophosphates, potassium phosphate -these are expensive fertilizers but are fully soluble and give immediate results.

Assimilable phosphoric acid salts aid plant growth, help regulate nutrition by fortifying them and are particularly beneficial to seed formation.

6. *Potash*

- Function

Potash is responsible for seed and fruit quality. It promotes sugar and starch formation. It reduces plant transpiration by retaining water in the cells, thus enabling the plant better to stand up to drought and frost.

- Sources

a) Organic refuse

All organic refuse, including vegetable ash, contains potash to varying degrees.

b) Potassic fertilizers

These include :

- Sylvinite, a low strength potassium chloride containing impurities in the shape of sodium chloride and magnesium.
- Potassium chloride, varying in strength from 49 to 60 % K_2O.
- Potassium sulphate, resulting from potassium chloride breakdown by sulphuric acid.

Chloride and sulphate must not be used indiscriminately for all crops ; tobacco, for example, requires a potassium sulphate based application, never potassium chloride.

Potash seems to play an essential role in the assimilation of carbonic gas and nitrates. It helps carry organic acids and improves the plant's resistance to disease. Its action is therefore a multiple one, and not just the direct action of the element itself.

5. MICRO-NUTRIENTS

These act at a homeopathic level. Like vitamins, they are indispensable, but an excess is definitely harmful.

Great care must be exercised if adding them to a compound fertilizer to ensure a homogeneous result.

6. ASSIMILATION BY THE PLANT

The principle of fertilizer assimilation by plants is not fully understood, but the use of radio isotopes offers a new technique for study of this process.

Absorption of a soluble substance by osmosis is comprehensible, but it is difficult to account for the fact that some insoluble substances pass through membranes and are found in plants.

Soluble fertilizers, being dispersed through the soil, have the advantage of being more readily accessible to roots.

The plant makes its own choice of nutrition, seeking within the range of its radicles the elements it requires. Successful assimilation depends on thorough spreading and if possible watering.

Plant roots secrete acids which solubilize non water-soluble substances.

Roots often penetrate deep into the soil and are able to draw up from below the elements required by the plant. Lucerne roots, for instance, have been found to reach a depth of 2.5 metres, and this is turned to advantage by farmers who rotate crops so as to get the best out of the soil.

7. SOIL pH

1. Soil pH

The extremes of soil pH recorded are 3.3 for acidity in FINLAND and 9.5 for basicity or alkalinity in EGYPT. These two levels are, however, exceptional.

In FRANCE farm land rarely has an acidity level below pH 5 or a basicity level above 8.5. Chalky soils are somewhere in the region of 8.

A slight variation in pH is enough to have a considerable effect on indigenous vegetation and on crop type.

2. Causes of soil acidity

Soil acidity is caused by the presence of H ions, which can be exchanged with other ions such as Ca, Na, etc..

In other words, if soil containing H ions is treated with a solution containing Ca ions, the H ions disappear, being replaced by the Ca ions. The converse is also true.

Exchange H ions in soil are mostly found in argillaceous or humic colloids.

3. Causes of acidification

Soil acidification is chiefly caused by the washing action of rainwater which carries lime carbonate -a neutralising agent- down to the lower layers, and also by accumulation of acid organic matter.

Farming, especially ploughing which brings the deeper layers up to the surface, and root activity have the effect of delaying soil acidification.

In fact, if cultivated land is compared with nearby uncultivated land, the difference is substantial, often some 2 to 3 pH units.

Nevertheless, with intensive farming the use of fertilizer is responsible for some acidification.

All the ammonia salts, sulphur and urea are acidifiers ; potassium salts, supers, lime and potassium nitrates and oilcake have no effect, while cyanamides, slag, sodium nitrate and basiphosphates are alkalizers.

4. *Plants and soil reactions*

Indigenous plant growth is an indicator of soil reaction. Some plants are typical of acid soils and others of alkaline soils.

The ideal growth condition for most cultivated plants is a more or less neutral soil. A number of plants can, however, tolerate slight acidity. Barley for instance is sensitive to acid, wheat somewhat less so, while oats and rye adapt to acid soils.

Beetroot grows at between 7 and 7.5 pH but at 6.5 pH yields diminish. The potato tolerates higher levels. Leguminous plants require a neutral or slightly alkaline soil with the exception of the lupin, the least sensitive of all to acidity, which grows in soils up to 6.5pH.

Many horticultural plants, such as pinks, chrysanthemums and cyclamen do best in acid areas ; a lot of flowers and shrubs prefer an acid soil and are grown in compost or heath-mould.

Soil reaction is also very important to microbial soil life. Ammonification -transformation of organic matter into ammonia, and nitrification - transformation of this ammonia into nitrate- take place when pH is between 7 and 8, i.e. in an alkaline environment. Nitrogen-fixing microbes (azotobacters) are no longer active once the pH falls below 6.

5. Consequences of soil acidity

As far as cultivated land is concerned, soil reaction has two consequences :

- it may or may not promote growth of some plants. As mentioned above, each plant has an optimum pH growth level.
- it has an effect on soil structure. Whenever a certain amount of clay is present in the soil it is vital, in order to make satisfactory structure and ease of labour, to have a sufficient amount of limestone, so that such a soil is basic or at any rate neutral.

  However, some alkaline soils can have an extremely poor structure, as for instance when calcium salts are replaced by sodium salts - sodium having the property of liquefying clay. Such soils are highly basic. This soil type occurs in EGYPT, ALGERIA and the CAMARGUE.

6. Neutralisation of acid soils

In practice only the application of lime or lime carbonate will make acid soils more neutral.

Liming should be moderate, even if this means increasing the frequency, and the application of organic matter, manure and manure crop should not be stinted.

7. Retention by the soil

The three basic fertilizers, nitrogen, phosphate and potash, react differently to rain and erosion in typical arable land.

Highly soluble nitrates are washed away by the first rainfall and thus lost to the crops. It is therefore preferable to spread them at the moment when they will be used by the plant, in small successive amounts.

Phosphoric acid is absorbed by the soil and spreads only over a small area of about 10 cm around the seed itself. It thus represents a store lasting several years which can be used by successive crops.

Potash, more solubre than phosphoric acid but less so than nitrates, spreads over an area of 35 cm during the year, so that each year ploughing brings it up into the arable layer where it is accessible to roots.

These are, however, not the only factors affecting salt dispersal in soil : alternating rain and drought cause saline solutions to sink and rise to the surface.

Retention varies greatly depending on soil type, being particularly efficient in argillaceous soil and peat, but very poor in sandy soil ; in the latter, fertilizer has a very fierce effect and plants should be "hand fed" in small, frequent doses.

1.2. THE MAIN FERTILIZERS

1. INTRODUCTION

Soil which supports plant life is basically composed of an organic frame (humus) and mineral salts.

Of the mineral salts the chief one is clay - 10 to 35 % depending on soil type. Clay is a sedimentary, silicate, aluminous rocks, basically composed of phyllite or fibrous minerals and formed by weathering of feldspathic rock (of a diameter greater than 2 microns). Limon is also found, with a diameter of 20 to 2 microns, and inevitably -in the form of mineral salts- various types of sand which are loose sedimentary rocks, most often quartz. Sand can be classed as gravel (diameter 200 to 20 microns) and coarse sand (2 to 200 microns).

Organic matter is basically composed of humus formed by lignin decomposition and micro-organisms.

Clay, in the shape of a colloid made up of hydrous alumina silicate, has a layered structure. Water molecules penetrate between the layers. Clay is adsorbent, and uses water to fix fertilizer solubles which are then passed on to the plant. This process is facilitated by Brownian motion.

The purpose of fertilizers is thus to restore to the soil menerals removed by crops and erosion. The soil type (pH) can be altered through organic or inorganic ameliorators.

Fertilizer may be applied either as such, in the form of inorganic chemicals, or in the form of natural fertilizer containing organic and inorganic components. The latter type was for many years the only kind of fertilizer used. Fertilizers can be divided into three categories :

- organic fertilizers
- natural inorganic fertilizers
- synthetic fertilizers.

2. ORGANIC FERTILIZERS

The main organic fertilizer is farmyard manure.

The so-called average content of farmyard manure is :

0.6 % total nitrogen

0.4 % phosphorus

0.5 % potash,

though in many cases it is less rich as a result of deterioration in storage.

The organic matter found in manure has a favourable effect on soil as it breaks it up, so that part of the soil mineral content becomes assimilable.

Other organic fertilizers include :

- dried blood
- human excrement
- wool waste
- bones, used either :
  - untreated : "green bones"
  - as bone ash
- oilseed oilcake
- compost (created by aerobic fermentation of household waste)
- guano.

Amounts of minerals put into the soil by this type of fertilizer are very small. Moreover, in the case of farmyard manure, for instance, its effect is only to put back into the soil part of what was taken out by the crops, thus keeping the soil properties constant without correcting any imbalance.

When organic fertilizer sources - generally of local origin - became insufficient they had to be supplemented by fertilizer of purely inorganic origin, and thus the inorganic chemical fertilizer industry grew up.

Inorganic chemical fertilizers provide the desired amount of fertilizer in proportions suited to each soil type and crop. They can be broken down into natural chemical fertilizers and synthetic inorganic chemical fertilizers.

3. NATURAL INORGANIC FERTILIZERS

Conversely to the above type, such fertilizers do not contain natural organic matter, yet are equally effective in enhancing soil fertility.

Natural fertilizer resources are abundant, but these are not directly usable by farmers. It is through the chemical industry that they can be developed for use.

Although potash is the most readily available of fertilizers, its recovery and purification require sizeable plant.

As regards nitrogen and phosphoric acid, substantial technical facilities are required to achieve an easily assimilated, easily handled form.

1. Potassic fertilizers

The only commercially produced agricultural fertilizers of this sort are chloride and sulphate, the effective ingredient being expressed in terms of oxide (K_2O).

The major sources of potassium salts, chloride in particular, derive from various rocks of carnallite, sylvite, kainite, leucite, polyhalite, etc.. type. Such potassium salts are generally formed by the concentration and drying up of a former sea.

Ores used particularly in the preparation of potassium chloride are hartsalz, sylvite and carnallite, in ascending order of importance.

Ore processing

Ore is crushed, may be magnetically separated, and is then sent to dissolution. If the ore contains a high proportion of magnesium salts, the first washes are treated with limewash, the quantity being calculated to ensure the following reaction :

$$Mg\,SO_4 + Ca\,(OH)_2 \rightarrow Ca\,SO_4 + Mg\,(OH)_2$$

The solution is filtered and sent to crystallization, the salts obtained being insoluble. By cooling a crystalline mass with about 56 % K CL is obtained after fining with a salt saturated solution, and after drying potassium chloride of 97 to 99 % K CL strength is obtained.

2. *Nitrogenous fertilizers*

Natural mineral nitrogen resources occur principally in the form of sodium nitrate, of which world supplies -concentrated virtually exclusively in CHILE- are insufficient to meet worldwide demand, and the distance from main consuming centres is a major drawback.

There are practically no natural minerals that contain ammoniacal nitrogen.

The solution was therefore to make use of the commonest source - the air, which contains 78 % elementary nitrogen that can be transformed into assimilable form.

3. *Phosphoric fertilizers*

Phosphorus is abundant in a natural state in the form of phosphates, but up to now only calcium phosphates have been used for agricultural purposes.

Fluorine is practically always associated with calcium phosphate, giving either crystallized compounds of the pure apatite type (as found in the KOLA peninsula) or elve amorphous varieties when other compounds are involved, CO_3Ca, etc..

Large deposits of these phosphorites occur in NORTH AFRICA and the U.S.A. particularly.

The apatite structure, characterised by the presence of fluorine in the phosphate molecule, means that it cannot be assimilated by plants, or at any rate only extremely slowly, unless it is very finely crushed and the soil is acid.

Thus emerged the notion of phosphoric acid assimilability - it was found from experience that in order to be assimilable P_2O_5 must be in an ionizable form ; this may be rendered by a number of phosphoric acid compounds, soluble either in water or in other media such as ammonium citrate solution.

Ground phosphates

The fertilizer value of unprocessed natural phosphates is still under discussion. Although they have the advantages of low cost price and the possibility of using low strength ore, with no chemical treatment, it must be remembered that consumption over the same area and for the same yield is markedly higher than in the case of superphosphate.

They are ground as finely as possible with the aim of being left with no more than 10 % tailings at 100 riddle size (160 microns).

Ground phosphate, being insoluble in water, is suited to moor and heathland, where the sandy, clayey humus contains little lime, or in acid prairies.

In such cases the acid root excretions are sufficient to dissolve the calcic salt, but it could not be applied to land used for rapid growth plants such as cereals.

Note that solubilisation of natural phosphates is distinctly activated when they are mixed with dolomite (5 to 10 %) and calcium sulphate.

Rock phosphate in a finely ground form may be used on moderately to strongly acid soils and particularly for long season or perennial crops with extensive root systems on acid soils in the tropics.

4. SYNTHETIC FERTILIZERS

1. Nitrogenous fertilizers

Ammonia is the basic raw material used for nitrogenous fertilizers. Nitrogen is generally known as the essential constituent of manuring. It is also the most expensive ingredient, hence the desirability of cutting down fertilizer costs for the same yield through use of a concentrated, active product.

Ammonia with a molecular weight of 17 contains 14g nitrogen in the gramme-molecule, its commercial strength being :

$$\frac{14}{17} \times 100 = 82\ \%\ \text{nitrogen.}$$

Its density in liquid state varies between 0.68 and 0.62 at 15°C. Boiling point at atmospheric pressure is -33°C. Ammonia can therefore be kept in liquid state only under pressure - the pressure varying according to temperature.

Temperature °C	-32	-5	0	+5	+15	+50
Pressure (bars)	1	3.5	4.2	5.1	7.2	20

Soil nitrogen, in order to be assimilated by plants, should be in nitric form. The ammoniacal form is, however, of some interest, in that through bacterial activity is gradually changes into an assimilable nitric form, the resulting fertilizer acting over a longer period of time.

Ammonia can be synthesized petrochemically, using hydrogen obtained from hydrocarbons and nitrogen taken from the air, and ammonia -as mentioned above- is the key to the synthesis of all other nitrogenous fertilizers.

Ammonia synthesis processes operate at different pressures and temperatures, but all the products obtained can be situated with reference to some point on the grade established in 1892 by LE CHATELIER.

Ammonia from a synthesis plant is recovered in liquid form and used directly in fertilizers. The main ammonia-based nitrate fertilizers are listed below :

- Used as such for nitrojection and liquijection
- Reacting with sulphuric acid, to yield ammonium sulphate
- Reacting with nitric acid to yield ammonium nitrate
- Used in the manufacture of compound N.P.K. fertilizers, either in nitric acid form or as such (ammonization)
- Oxidized to produce nitric acid which in turn is used :
  - in ammonium nitrate
  - in lime nitrate
  - in compound fertilizer manufacture
- Used with residual CO_2 from ammonia synthesis to produce urea
- Used in the manufacture of liquid fertilizers.

2. *Effect of synthetic nitrogenous fertilizers - Brief description of their manufacture*

a) Ammoniacal fertilizers

Ammoniacal fertilizers may be divided into the following types :

- Ammonium sulphate, obtained by direct reaction of ammonia on sulphuric acid within a sulphate solution. The resulting supersaturation leads to the formation of crystals, which are dried before being sent to the silo.
- Urea is obtained from the reaction of ammonia with carbon dioxide in synthesis autoclaves under 180 to 200 bar pressure and at a temperature of about 185°C. Manufacture comprises an intermediate stage, that of ammonium carbamate which by dehydration yields urea. After being condensed and filtered the concentrated urea solution is pulverized at the top of a prilling tower.

- **Effect** : the effect of ammoniacal fertilizers proper is progressive and continuous, as the nitrification process takes place over a period of time. They are retained by the soil's power of absorption and are especially effective against winter soil leaching.

b) Nitrate fertilizers

The main fertilizers of this type are lime and sodium nitrate.

- **Sodium nitrate**

  This is no longer used.

- **Lime nitrate**

  Lime nitrate is released in the form of a solution when natural phosphates used in compound fertilizer manufacture reacted with nitric acid. The salt is crystallized by cooling and centrifugally separated.

- **Effect**

  Nitrate fertilizers being highly soluble are at once absorbed by the soil. As no previous microbial transformation is required, they are very rapidly assimilated by plants, hence their particular value when swift action is indicated, as in the case of late spreading.

c) Ammonia-nitric fertilizers

This category includes the various ammonitrates and ammonium nitrate.

- **Ammonitrates**

  - Rich ammonitrate (33.5 %) obtained by coating ammonia nitrate granules with chalk.

  - 22 % ammonitrate, which contains a greater quantity of lime carbonate.

- Ammonium nitrate with 34.8 % nitrogen

The basic ammonium nitrate solution is obtained by direct reaction of gaseous ammonia with nitric acid. The solution is then concentrated, and pulverized into fine droplets at the top of a granulation tower. As they fall the droplets are solidified on meeting rising cold air.

- Effect

These fertilizers are the most popular with consumers in EUROPE. The association of ammonia and nitric acid means that the agronomic properties of the two fertilizers can be combined in one substance.

Nitrate nitrogen, the first to be absorbed, acts very swiftly. The ammonia nitrate, on the other hand, is fixed by the soil's power of absorption and released gradually. Ammo-nitrates are thus very versatile in use.

d) Compound fertilizers

The three basic elements - N.P.K. - must be put back into the soil, but most fertilizers contain only one of these elements.

Moreover, a simple fertilizer (one which is either nitrogenous, phosphatic or potassic) is efficacious only if a sufficient quantity of the other essential nutritive elements is already present in the soil.

Should this not be so, the application of a simple fertilizer represents needless expense and may even lead to a drop in yield. Manuring must therefore be complete and balanced, and this is achieved by use of compound fertilizers containing the three important elements : nitrogen, phosphorous and potassium (N.P.K.).

Each crop's fertilizer requirements are different, as regards both total quantities and speed of absorption during growth.

This would appear to restrict N.P.K. fertilizers to a small number of formulae only. However, such is far from being the case.

In fact soils on account of their absorption facility are able to store phosphore potash and lime, in varying amounts and for differing lengths of time. With regard to the above elements the aim of dressings is to maintain or build up the quantity of each stored by the soil rather than to match the supposed needs of any one crop. This unfortunately does not apply to inorganic nitrogen which most soils do not store well, so that additional applications of fertilizer have to be matched to crop growth patterns.

This state of affairs warrants meeting needs by applying just the right amount of nitrogen for present requirements together with phosphate and potash in quantities designed to match the average needs of several crops, where crop rotation is practised following a planned cycle.

It has been found from experience that in most cases a small number of carefully selected formulae provides all that is required in the way of plant nutrition and at the same time maintains soil fertility.

The use of formulae relatively rich in P as against N offers a means in some cases of further relaxing the matching of the nitrogenous component to growth requirements, particularly when the latter are especially subject to meteorological conditions and cultivating practices.

In view of the very composition of compound fertilizer, with the obligatory association of nitrate nitrogen and phosphatic compounds, the advantages became apparent of manufacturing a fertilizer where natural phosphate P_2O_5 solubilisation is achieved through nitric acid instead of sulphuric acid.

Benefits are threefold :

- Savings of sulphuric acid
- avoidance of the large calcium sulphate part, resulting in a more concentrated fertilizer
- the fertilizers in the end-product are no longer merely roughly mixed but are closely combined at molecular level.

e) Fertilizer in solution

Such fertilizers, whether nitrogenous, binary or ternary, are concentrated solutions of classic fertilizers (urea, ammonium nitrate, sulphate, phosphoric acid, etc..). They are the most recent to become available for agricultural use, and the versatility of their formulae and grades make them the fertilizers of the future for sophisticated agriculture.

Liquid fertilizers may be classed as follows :

- Vapour pressure solution

  Such products contain ammonia and must therefore be stored in sealed containers. They fall into two types :

  - ammoniawater with a low nitrogen density, obtained by dissolution of ammonia gas in water.
  - composite solutions of salts and ammonia in water (Barett liquors). These usually contain urea and/or ammonium nitrate in solution. The nitrogen density can be increased by bubbling ammonia gas in the solution.

- Solution without vapour pressure

  Such solutions are the most widely used in FRANCE. Unlike the liquid fertilizers described above, these clear solutions may be stored and handled in the open with no hazard to personnel and no risk of nitrogen loss. This category covers many possibilities:

  - Nitrogenous solutions : these vary in nitrogen density from 20 to 40 kg of nitrogen per 100 litres. They contain urea, ammonium nitrate and/or ammonium sulphate.
  - Binary N.P solutions : phosphoric acid is mainly obtained from ammonium phosphate. Depending on whether the base is phosphoric acid of superphosphoric acid - a blend of ortho -and polyphosphoric acids- the basic formula is more or less concentrated : 10 kg of nitrogen and 30 kg of P_2O_5 per

  100 litres using phosphoric acid, and 14/48 with superphosphoric acid. From 14/48/0 and urea or ammonium nitrate a number of binary formulae can be derived, e.g. 20/10/0, 17/17/0, etc..

  - Ternary N.P.K. solutions : a large number of formulae may be prepared. Nitrogen is obtained from ammonium phosphate or urea, phosphoric acid from 10/48/0 and potash from potassium chloride or sulphate.

- Supersaturated solutions

  These are suspensions, or muds, obtained by taking concentration beyond saturation limits. Various products -for instance, colloidal clay- are added to the suspension to inhibit crystallization.

  Such fertilizers may also be obtained by direct reaction, yielding finely divided solid compounds which are maintained in suspension. In the latter case raw materials need not be the same as for clear solutions.

3. Synthetic phosphoric fertilizers

The whole phosphatic fertilizer industry is based on the transformation of natural phosphates (tricalcic phosphate $(PO_4)_2 Ca_3$) into compounds which can be assimilated by plants (monocalcic phosphate or phosphonic acid which is further converted to MAP or DAP.
It would seem that the phosphoric molecule is assimilable in its simple form but not in the compound (fluo-phosphoric or apatite) state i.e. natural phosphates which mostly have a $\frac{F}{P_2O_5}$ ratio greater than 0.0891 - equivalent to pure apatite $3 (PO_4) 2CA F_2Ca$. The fertilizer industry therefore seeks to release the anhydride from its fluorine compound by either direct attack (by a strong acid) or heat treatment.

Once the fluorine compound has been broken down, the anhydride becomes assimilable and retains this property, even after insolubilisation in the soil, provided that it is not accompanied by a return to a compound state.

Chalky soil is improved by liming and the phosphatic fertilizer remains assimilable, whether in soluble from or not ; in an acid soil which generally contains sesquioxides it is partly transformed into iron phosphate and aluminium.

Phosphatic fertilizers may be classed in four categories :

- crushed natural phosphates (reffered to as ground)
- simple and triple superphosphates
- bone superphosphates
- basic slag.

There is more call for superphosphate (super of triple) in which monocalcic phosphate and sulphate predominate, than for the "ground phosphates". Their degree of assimilation appears markedly higher.

Phosphate type	% P_2O_5	Assimilation	Effect on the soi
"Double"superphosphate	44	95	neutral
Ordinary superphosphate	14 - 16	90	neutral
Basic slag	18	80	alcaline
Bone ash (4 % N_2)	20	70	alcaline
Crushed natural phosphats	30 - 35	25	alcaline
Apatite	38 - 42	25	alcaline

- Superphosphates

  This name refers to the result of natural phosphate and bone ash attack by sulphuric acid (53° B_2, or 66/68 % SO_4H_2).

  Sulphuric acid tends to have the effect of transforming insoluble tricalcic phosphate into monosoluble phosphate.

  If instead of using a fairly small quantity of sulphuric acid on the natural phosphate (1T/1T), a triple quantity of acid is usde, phosphoric acid is obtained in a concentrated solution together with plaster, which is removed by filtration. Large amounts of sulphuric acid are used in this process, hence the accent in industry on decreasing or eliminating sulphuric acid consumption for natural phosphate solubilization.

Various processes are in use. In thermal treatment for example two methods are available :

- Phosphoric acid can be prepared by reducing natural phosphate with coal in the presence of silica in an electric oven, the phosphorous obtained being oxidized in air.

  The phosphoric acid obtained is pure, but a large amount of electricity is consumed in its manufacture.

- Calco-alkaline phosphate may be prepared by substituting a alkaline metal, such as soda, potash, etc.. for part of the natural phosphate lime.

  This reaction takes place in presence of silica. The required temperature is not so high as in phosphoric acid manufacture, but is still fairly high, and this process is not very widely used (defluorised phosphate).

  There is another process in which natural phosphate is corroded by hydrochloric acid, obtained as a by-product of sodium chloride electrolysis or potassium sulphate manufacture, for example, the phosphoric acid then being precipitated by limewash. The result is bicalcic phosphate, an excellent fertilizer (precipitated phosphate).

• Concentrated double or triple superphosphate

The P_2O_5 content of such fertilizers may be as high as 50 % ; their manufacture is similar to that of "super", a phosphoric acid solution taking the place of the sulphuric acid in the natural phosphate treatment.

- Enriched superphosphates

Sulphuric acid with phosphoric acid added at the natural phosphate attack stage yields enriched superphosphates with 22 to 29 % P_2O_5.

- Ammonium-phosphates

Phosphoric acid can also be used to manufacture mono-ammonium or diammonium-phosphate, which is a base for very high fertilizer content compound fertilizers.

The following compositions may be obtained :

RATIO		FORMULA
Binary fertilizers		
from PO_4H_3 and NH_3 alone	1. -1.5 - 0	23 - 33 - 0
	1. 2.5 - 0	18 - 46 - 0
	1. 3.0 - 0	16 - 48 - 0
	1. 4.3 - 0	11 - 48 - 0
adding NO_3NH_4	1. 0.5 - 1	19 - 9.5 - 19
	1. 0.7 - 1	18 - 12.6 -18
	1. 1.5 - 1	16 - 24 - 16
Ternary fertilizers		
with ClK PO_4H_3	1. 0.5 - 1	19 - 9.5 - 19
	1. 0.7 - 1	18 - 12.6 - 18
	1. 1.0 - 1	17 - 17 - 17
	1. 1.0 - 1	14 - 14 - 14
	1. 1.5 - 1	16 - 24 - 26

- High P_2O_5 content phosphoric acid (superphosphoric)

Other processes used, still with the aim of increasing the P_2O_5 content, involve treating so-calles "green" phosphoric acid by vacuum evaporation or hot gas bubbling, or in some cases by plunging a flame. The result is a superphosphoric acid, containing approximately :

50 %	ortho acid	PO_4H_3
33 %	pyro acid	$P_2O_7H_4$
17 %	meta acid	PO_3H

- Bone_superphosphates

Since natural phosphate deposits began to be worked, bone-based fertilizers have been manufactures using only waste, in most cases after the ossein recovery stage.

The "bone super" and bone phosphate industries are very small scale.

- Basic_slag

When phosphorated iron is processed in a basic-lined furnace with ores similar to Lorraine minette, a 37/45 % $(PO_4)_2Ca_3$ by-product is obtained. Such slag agrees to quite a degree with a silico-carnotite formula $(PO_4)_2Ca_3$, SiO_3Ca, CaO.

In the case of these fertilizers, assimilability is defined not by solubility in ammonium citrate as in the case of phosphates and supers, but by their solubility in Wagner's reagent (2 % citric acid).

The method used to render slag into fertilizer form usually involves two successive crushing operations.

The first crushing yields a product from which the iron has been removed by means of a magnetic separator and which leaves 30 % tailings.

The second crushing produces commercial fertilizer 75 % siftable at riddle size 100 (170 microns).

P_2O_5 strenght varies from 14 to 20 %. This type of fertilizer is successful in clayey and acid soils and makes a good ameliorator.

Also included in this category are certain calcined phosphates, produced in a rotary furnace by roasting a mixture of ore (100 parts), sodium sulphate (15 parts) and coal (15 parts). Nominal strength varies between 23 and 25 % P_2O_5 and such fertilizers in blends with others are suited to acid soils.

4. Potassic fertilizers

Potassium chloride and sulphate alone are used for agricultural purposes. These are the only two salts includes in the class of natural inorganic fertilizers, although there is an industrial process which separates the various salts associated with KCL, the most in demand.

Agriculture accounts for 90 to 92 % of all chlorides and sulphates, most of which are obtained from deposits.

Potassium sulphate may be manufactured in combination with phosphate. Hydrochloric acid released by sylvinite acid attack is used to decompese natiral phosphates. The resulting phosphoric acid solution is neutralized with limewash, and yields bicalcic phosphate.

5. Direct use of anhydrous ammonia as fertilizer (liquifection)

By virtue of its composition ammonia is the richest of the nitrogen fertilizers, with 82.3 % nitrogen.

As such it can be used only by direct application to the soil. Depth depends on :

- soil type
- the crop to be fertilized
- the spreading date

and is generally somewhere between 8 and 25 cm.

As soon as ammonia is injected into the soil it changes from a liquid to a gaseous state. This enhances its dispersal, but is governed by the soil type, dispersal being greater in a light, dry soil than in a heavy, damp one. The dispersal area is assumed to extend to 10-15cm from the point of injection.

As to its assimilation there are a few points to be noted, nitrification in particular. NH_4 + ammonia ions are more swiftly nitrified. The increased pH due to injection favours microbial activity.

The change in soil pH is only temporary, and is limited to the soil's neutralising power. The pH value gradually returns to normal as nitrification takes place.

The ammonia gas diffuses in a regular manner around the point of injection, over an area of 10-15 cm, and is fixed homogeneously by the soil. The attraction is so strong that even a copious water leaching will not carry away the ammonia in spite of its solubility. This would not be the case with NO_3-anions. With ammonia there is a phenomenon of true absorption : a soil sample taken a few minutes after injection is already free from the suffocating ammonia smell.

The ammonia is released progressively through soil humidity, and the NH_4+ ion can act as a fertilizer, either directly on the plant while in the ammoniacal state or after transformation by microbial action into nitric nitrogen. This nitrification is governed by humidity, soil aeration, pH, the quantity of organic matter and most important, temperature.

2. THE FERTILIZER INDUSTRY

GROWTH

The fertilizer industry has been growing steadlily and rapidly since the beginning of this century, as can be seen from the table which follows :

	PRODUCTION (1) Million tons NPK	CONSUMPTION (2)
1905/06	2.0	1.9
1913/14	4.1	3.9
1919/20	3.7	3.5
1938/39	3.7	9.3
1945/46	7.9	7.5
1949/50	14.1	13.6
1959/60	29.1	27.8
1969/70	66.2	62.9
1973/74	87.9	83.6
1974/75	91.8	80.9
1975/76	92.2	88.7

Source : FAO production year book

(1) *The ratio of NPK to end products is about 1/2.5, i.e. the 91.8 million tons of NPK manufactures in 1974/75 represent some 250 million tons of finished fertilizer.*

(2) *The gap between production and consumption is largely accounted for by products in the distribution stage, and losses.*

As output increased, quality changes were also taking place. During the early years -from 1906 to 1939- most commercial fertilizer was organic, and mainly took the form of meat industry by-products e.g. dried blood, bones, scraps. From 1945 onwards, however, synthetic and inorganic matter began increasingly to represent the bulk of fertilizer so that today organic materials account for only a very small proportion of the total.

Since output in 1946 was less than 10 % of present output, it can be concluded that most existing production capacity was built after the second world war. Table 1.2 breaks down production between developed and developing countries. The latter today produce 15 % of world fertilizer demand (20 % nitrogen, 16 % phosphate, 3 % potash).

PAST CONSUMPTION

Fertilizer consumption statistics are given in tables1.3to1. and figure 1.1. Table 1.3 shows consumption of each nutrient in developed and developing countries, between 1950 and 1976. In 1976 for example respective shares (%) were :

	N	P_2O_5	K20	NPK
Developed countries	71	78.6	89	77.3
Developing countries	29	21.4	11	22.7

Details of consumption in 78 countries are presented in table 1.4.

taking 1976 as an example, the highest consumers were :

NPK (million tons)	
U.S.A.	18.84
U.S.S.R.	16.18
CHINA	6.2
FRANCE	4.64
POLAND	3.65

N (million tons)	
U.S.A.	9.38
U.S.S.R.	7.35
CHINA	4.55
INDIA	2.03
FRANCE	1.7

Table 1.5 and figure 1.2 show consumption per head in 78 different countries in 1975/76. In JAPAN consumption was fairly low -16 kg per head- while CUBA with 35 kg per head had the highest of the developing countries. CHINA with 7.3 kg per head, reached a markedly higher level than INDIA where the figure was 4.5 kg/head.

It can be seen from the table 1.5 that in 27 developing countries consumption was less than 5 kg/head, which in most cases is far too low to fertilize the crops required to feed the population adequately. The only exceptions are ARGENTINA, THAILAND and BURMA where population density is low.

Table 1.6 gives consumption per hectare of cultivated land in 78 different countries, for 1975/76. In looking at these figures it must be remembered that in many countries a certain amount of fertilizer goes to permanent pasture, not to crops. This is the case in HOLLAND, BELGIUM, WEST GERMANY, FRANCE, DENMARK, the UNITED KINGDOM, AUSTRALIA and NEW ZEALAND.

It is also seen from this table that 28 of the developing countries have a per hectare consumption of less than 20 kg and 19 less than 10 kg i.e. they are virtually non-users.

The aim in compiling table 1.7 was to show the largest producers, consumers, and surpluses and deficiencies of nitrogenous , phosphate and potassic fertilizers in the World in 1973/74. The UNITED STATES was overall the largest producers, and the largest consumer of potash. The USSR was the largest producer and second largest consumer of nitrogen and phosphate, and the largest potash producer. JAPAN had the greatest surplus of nitrogen, the UNITED STATES of phosphate and CANADA of potash. CHINA had the greatest deficiency of nitrogen, FRANCE of phosphate and the UNITED STATES of potash.

Only a few developing countries appear in the list of major producers, but a great number among those with the largest deficiencies.

Figure 1.4 shows fertilizer consumption trends over the 1955-1976 period. Consumption grew steadily over this time, in both developed and developing countries.*

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* *The one exception was 1974/75 when for the first time since 1945 there was a drop in consumption, brought about by a sudden rise in nutrient prices.*

Since the fertilizer industry is relatively young, in that the rapid expansion from 1945 onwards was matched by fundamental qualitative changes, it might be somewhat misleading to view its growth as continuous through time. There are now grounds for considering that a structural break occurred in the early nineteen-sixties as a result of the population explosion and the consequent demand for food.

The rapid world population increase in the nineteen-fisties compared to previous decades is illustrated by the following data :

	Population growth (millions)
1920/30	200
1930/40	230
1940/50	261
1950/60	485

This rapid growth in the nineteen-fifties led to new pressure on world food supplies and prices in the early sixties. The impact was not felt until 1960 thanks to record harvests in 1958 and 1960.

Then in 1961 cereal crops were very poor, 2.9 % less than in 1960, the greatest percentage drop in the history of our time. This fall, which hit the UNITED STATES, CANADA, EUROPE and OCEANIA hardest, brought about a revolution in world agricultural growth, including the use of fertilizers and grain production, which first started in the developed countries in 1961/62 and spread to the developing countries in 1962/65. New processes and new technology for large scale fertilizer production came successively on to the market, thus laying the foundations for the growth of a modern chemical fertilizer industry. This new pattern of growth still continues.

It can be seen from figure 1.5 that in world consumption terms nitrogen has a much higher growth rate than P_2O_5 and K20, the latter two keeping parallel.

UP to 1955 the nitrogen share was lower than either P_2O_5 or K20. The percentage grew steadilv in the developed countries from 30 % in 1955 to 45 % in 1976.

The nitrogen percentage in developing countries has remained fairly constant, in the 53-63 range, but is now beginning to show a gentle decline.

TABLE 1.2 - WORLD FERTILIZER PRODUCTION - HISTORICAL DATA 1950-1975 (MILLIONS OF TONS)

	Developing countries				Developed countries			
	N	P_2O_5	K_2O	NPK	N	P_2O_5	K_2O	NPK
1950	0.35	0.27	0.01	0.63	3.73	5.59	4.21	13.5
1951	0.43	0.34	0.02	0.79	4.25	5.93	4.94	15.1
1952	0.45	0.36	0.02	0.83	4.49	6.13	5.40	16.0
1953	0.51	0.37	NIL	0.88	5.02	6.16	5.87	17.1
1954	0.59	0.41	0.01	1.01	5.59	6.60	6.32	18.5
1955	0.58	0.45	0.02	1.05	6.29	7.34	6.84	20.5
1956	0.59	0.54	0.04	1.17	6.94	7.71	7.14	21.8
1957	0.72	0.56	0.06	1.34	7.49	7.94	7.65	23.1
1958	0.77	0.60	0.09	1.46	8.24	8.20	7.66	24.1
1959	0.85	0.64	0.10	1.60	9.00	8.68	8.17	25.9
1960	0.93	0.72	0.12	1.77	9.43	9.24	8.61	27.3
1961	1.04	0.79	0.14	1.97	10.37	9.58	8.66	28.6
1962	1.14	0.76	0.14	2.04	11.12	9.86	9.25	30.2
1963	1.43	0.85	0.16	2.44	12.2	10.5	9.69	32.4
1964	1.72	1.01	0.19	2.92	13.6	11.7	10.8	36.1
1965	2.02	1.15	0.30	3.47	15.4	12.7	11.8	39.9
1966	2.24	1.30	0.39	3.93	17.7	14.2	13.4	45.3
1967	2.49	1.48	0.38	4.35	19.8	15.3	14.1	49.2
1968	2.79	1.75	0.41	4.95	22.4	16.0	14.8	53.2
1969	3.44	2.01	0.43	5.88	24.9	16.3	15.4	56.6
1970	4.07	2.32	0.59	6.98	26.1	17.0	16.1	59.2
1971	4.59	2.59	1.00	8.18	28.3	18.2	16.9	63.4
1972	5.61	3.11	1.13	9.85	29.3	19.3	18.3	66.9
1973	6.61	3.54	1.22	11.4	31.2	20.1	19.0	70.3
1974	7.24	3.97	1.10	12.3	33.3	21.2	21.1	75.6
1975	7.99	4.22	1.25	13.5	34.3	21.5	22.5	78.3
1976	8.77	3.9	0.6	13.27	35.1	21.0	22.9	79.0

Source : FAO production Year book

TABLE 1.3- WORLD FERTILIZER CONSUMPTION - HISTORICAL DATA, 1950-75 (MILLIONS OF TONS)

	Developing countries				Developed countries			
	N	P_2O_5	K_2O	NPK	N	P_2O_5	K_2O	NPK
1950	0.56	0.36	0.09	1.01	3.19	5.41	4.04	12.6
1951	0.59	0.41	0.11	1.12	3.73	5.81	4.43	14.0
1952	0.68	0.48	0.14	1.30	4.01	5.77	4.86	14.6
1953	0.87	0.51	0.15	1.53	4.60	6.08	5.20	15.9
1954	0.96	0.60	0.19	1.75	5.18	6.51	5.48	17.2
1955	0.94	0.60	0.23	1.78	5.69	7.14	6.11	18.9
1956	1.24	0.66	0.27	2.17	5.82	7.45	6.51	19.8
1957	1.45	0.76	0.31	2.52	6.19	7.66	6.87	20.7
1958	1.58	0.83	0.35	2.76	6.69	7.87	7.08	21.6
1959	1.81	0.86	0.38	3.04	7.47	8.38	7.56	23.4
1960	1.95	0.94	0.42	3.31	7.80	8.90	7.83	24.5
1961	2.45	1.05	0.54	4.04	8.51	9.03	7.90	25.5
1962	2.49	1.10	0.54	4.12	9.15	9.51	8.15	26.8
1963	2.77	1.27	0.56	4.61	10.4	10.1	8.78	29.3
1964	3.33	1.47	0.68	5.48	11.7	11.0	9.36	32.1
1965	3.65	1.58	0.73	5.95	12.8	12.2	10.3	35.3
1966	4.23	1.77	0.84	6.84	14.7	13.0	11.4	39.1
1967	5.33	2.11	1.00	8.44	16.5	13.9	12.0	42.5
1968	5.51	2.34	1.12	8.97	18.5	14.5	12.9	45.9
1969	6.80	2.81	1.34	11.0	19.7	15.2	13.4	48.3
1970	7.70	3.25	1.47	12.4	21.0	15.6	14.0	50.5
1971	8.77	3.51	1.80	14.1	23.0	16.3	14.9	54.2
1972	9.45	4.09	1.93	15.5	23.8	17.0	15.7	56.5
1973	10.6	4.59	2.24	17.4	25.2	18.0	16.6	59.8
1974	11.4	5.34	2.61	19.3	27.3	18.9	18.1	64.3
1975	11.7	5.49	2.85	20.0	27.2	17.4	17.1	61.7
1976	12.6	5.17	2.37	20.14	30.7	18.9	18.97	68.57

TABLE 1.4 - FERTILIZER CONSUMPTION 1973/74

Includes all countries with population of over 5 million in 1976

Listing is in order of NPK consumption

COUNTRIES	N	P_2O_5	K_2O	NPK
	(Thousands of tons of nutrients)			
1. United States	3 384	4 731	4 725	13 840
2. USSR	7 357	3 833	4 397	15 187
3. China	4 550	1 253	401	6 209
3. France	1 707	1 618	1 314	4 640
5. Poland	1 223	942	1 491	3 656
6. Germany (Fed. Rep)	1 228	780	1 098	3 106
7. India	2 031	453	270	2 754
8. Brazil	410	915	588	1 912
9. United Kingdom	1 045	391	399	1 835
10. Germany (Dem. Rep)	678	400	706	1 784
11. Japan	638	624	517	1 779
12. Czechoslovakia	511	476	667	1 654
13. Hungary	536	429	553	1 518
14. Spain	753	422	257	1 443
15. Italy	724	490	276	1 490
16. Canada	562	526	215	1 303
17. Romania	788	338	71	1 197
18. Mexico	833	220	48	1 101
19. Korea (Rep. of)	488	236	161	885
20. Turkey	453	373	15	842
21. South Africa	285	343	127	755
22. Australia	165	490	73	728
23. Yugoslavia	360	197	163	720
24. Bulgaria	380	250	50	679
25. Denmark	339	129	171	639
26. Netherlands	451	79	101	631
27. Pakistan	442	101	2	545
28. Sweden	257	141	128	523
29. Egypt	415	83	3	501
30. Indonesia	342	117	25	483
31. Belgium	182	144	148	474
32. Greece	275	160	28	463
33. Korea (DPR)	264	125	45	434
34. Iran	194	142	4	341
35. Vietnam	204	100	36	340
36. Cuba	156	62	36	340
37. Austria	121	74	115	310
38. Portugal	141	74	30	245
39. Philippines	133	40	49	222
40. Colombia	131	47	38	216
41. Bangladesh	151	51	13	215
42. Malaysia	72	30	94	195
43. Thailand	79	62	39	180
44. Morocco	63	65	35	163
45. Algeria	63	77	23	162
46. Rhodesia	75	45	37	157

TABLE 1.4 (CONTINUED)

COUNTRIES	N	P_2O_5	K_2O	NPK
47. Venezuela	65	41	34	140
48. Switzerland	42	38	38	138
49. Peru	82	12	2	96
50. Sudan	35	-	-	35
51. Chile	39	47	8	94
52. Syria	42	21	2	65
53. Sri Lanka	38	11	16	64
54. Argentina	28	22	5	55
55. Nigeria	30	16.1	6	52
56. Guatemala	30	15	4	49
57. Tunisia	18	26	5	49
58. Kenya	20	21	3	44
59. Burma	35	6.5	0.8	43
60. Ecuador	20	13	6	39
61. Afghanistan	28	8	-	36
62. Iraq	25	7	1	33
63. Ethiopia	13	20	-	33
64. Tanzania	15	11	4	30
65. Ghana	14	8.9	5.1	28
66. Cameroon	6	3	2	12
67. Nepal	8	2.5	0.8	12
68. Saudi Arabia	5.7	2.3	1.3	9.3
69. Yemen (AR)	3.3	1.3	-	6
70. Madagascar	4	1.5	0.5	6
71. Mozambique	4	1.6	0.4	5.7
72. Uganda	1.4	3.3	0.5	5.2
73. Zaire	2.6	0.6	1.9	5.1
74. Angola	2	1.3	0.7	4.0
75. Bolivia	1.6	1.5	0.1	3.2
76. Mali	1.8	0.4	-	2.2
77. Kampuchea	1.2	0.5	-	1.7
78. Upper Volta	0.4	0.4	-	0.8
Developped countries	30 693	18 888	18 980	68 572
Developing countries	12 605	5 157	2 357	20 108
world total	43 298	24 045	21 337	88 680

Source : FAO Production yearbook 1978

TABLE 1.5 : FERTILIZER CONSUMPTION PER CAPITA 1975

Includes all countries w ith population of over 5 million in 1975
(kg of NPK/capita)

1.	Hungary	144.1	41.	Syria	9.0
2.	Denmark	126.1	42.	Tunisia	8.5
3.	Czechoslovakia	111.8	43.	Colombia	8.3
4.	Poland	108.0	44.	Guatemala	8.1
5.	Germany (Dem. Rep)	104.2	45.	Vietnam	7.8
6.	United States	88.1	46.	Pakistan	7.7
7.	France	87.7	47.	China	7.3
8.	Bulgaria	77.7	48.	Peru	6.3
9.	Sweden	63.8	49.	Ecuador	5.5
10.	USSR	63.5	50.	Sudan	5.2
11.	Canada	57	51.	Philippines	5.0
12.	Romania	56.5	52.	Sri Lanka	4.6
13.	Australia	53.6	53.	India	4.5
14.	Greece	51.8	54.	Thailand	4.3
15.	Germany (Fed. Rep.)	50.4	55.	Indonesia	3.6
16.	Belgium	46.6	56.	Kenya	3.4
17.	Netherlands	46.3	57.	Irak	3.0
18.	Austria	41.1	58.	Bangladesh	2.9
19.	Spain	40.9	59.	Ghana	2.8
20.	Cuba	35.0	60.	Argentina	2.2
21.	Yugoslavia	33.8	61.	Afghanistan	1.9
22.	United Kingdom	32.4	62.	Cameroon	1.9
23.	South Africa	30.6	63.	Tanzania	1.9
24.	Portugal	27.9	64.	Mozambique	1.6
25.	Korea (DPR)	27.5	65.	Burma	1.4
26.	Italy	26.8	66.	Ethopia	1.2
27.	Rhodesia	25.0	67.	Nepal	1.0
28.	Korea (Rep of)	25.0	68.	Saudi Arabia	1.0
29.	Switzerland	21.2	69.	Yemen (AR)	0.9
30.	Turkey	21.1	70.	Nigeria	0.8
31.	Mexico	18.6	71.	Madagascar	0.7
32.	Brazil	17.4	72.	Argola	0.6
33.	Japan	16.0	73.	Bolivia	0.6
34.	Malaysia	15.	74.	Uganda	0.5
35.	Egypt	13.3	75.	Mali	0.4
36.	Venezuela	11.4	76.	Kampuchea	0.2
37.	Iran	10.4	77.	Upper Volta	0.2
38.	Algeria	9.7	78.	Zaire	0.1
39.	Morocco	9.3			
40.	Chile	9.2			

Developed countries average	53.0
Developing countries average	6.8
World average	22.3

TABLE 1.6 : FERTILIZER CONSUMPTION PER HECTARE - 1975 OF ARABLE LAND AND PERMANENT CROPS

Includes all countries with population of over 5 million in 1976
(kg of NPK/ha)

1.	Netherlands	750
2.	Belgium	540.4
3.	Germany (Fed. Rep.)	385.5
4.	Germany (Dem. Rep.)	361.5
5.	Switzerland	358.3
6.	Korea (Rep of)	357.9
7.	Japan	319.3
8.	Czechoslovakia	314.7
9.	Hungary	278.3
10.	United Kingdom	282.9
11.	France	246.7
12.	Poland	242.0
13.	Denmark	239.4
14.	Korea (DPR)	201.8
15.	Austria	192.8
16.	Sweden	173.6
17.	Bulgaria	156.5
18.	Egypt	131.2
19.	Italy	121.0
20.	Greece	119.0
21.	Romania	114.0
22.	Cuba	107.1
23.	United States	90.0
24.	Yugoslavia	89.6
25.	USSR	69.7
26.	Spain	69.3
27.	Portugal	67.6
28.	Rhodesia	63.3
29.	Vietnam	61.0
30.	Malaysia	53.0
31.	Brazil	52.3
32.	South Africa	52.1
33.	China	48.1
34.	Colombia	42.1
35.	Mexico	39.3
36.	Sri Lanka	32.5
37.	Canada	29.8
38.	Turkey	29.8
39.	Peru	29.7
40.	Guatemala	28.5
41.	Philippines	28.1
42.	Pakistan	28
43.	Venezuela	26.2
44.	Indonesia	26.0
45.	Kenya	25.2
46.	Algeria	23.0
47.	Bangladesh	22.6
48.	Morocco	21.4
49.	Iran	20.7
50.	India	16.5
51.	Chile	16.2
52.	Australia	15.9
53.	Sudan	12.7
54.	Syria	11.8
55.	Saudi Arabia	11.6
56.	Tunisia	11.2
57.	Thailand	10.9
58.	Ghana	10.3
59.	Ecuador	9.1
60.	Iraq	6.3
61.	Nepal	6.1
62.	Tanzania	4.9
63.	Afghanistan	4.3
64.	Burma	4.1
65.	Yemen (AR)	3.8
66.	Angola	2.2
67.	Nigeria	2.2
68.	Madagascar	2.1
69.	Mozambique	1.9
70.	Cameroon	1.7
71.	Argentina	1.6
72.	Bolivia	1.0
73.	Uganda	1.0
74.	Zaire	0.7
75.	Kampuchea	0.6
76.	Mali	0.2
77.	Upper Volta	0.1

Developed countries average	100.4
Developing countries average	23.0
World average	5.89

Source : FAO yearbook 1976

TABLE 1.7.- FERTILIZER - COUNTRY ANALYSES, 1973/74 - LARGEST PRODUCERS, CONSUMERS, SURPLUSES AND DEFICITS

A - NITROGEN FERTILIZER (THOUSANDS OF TONS OF N)

PRODUCERS		CONSUMERS		SURPLUSES		DEFICITS	
1. United States	9.152	1. United States	8,277	1. Japan	1.341	1. China	1,084
2. USSR	7,241	2. USSR	6,256	2. USSR	985	2. India	785
3. China	2,731	3. China	3,815	3. United States	875	3. Egypt	329
4. Japan	2,162	4. India	1,835	4. Netherlands	816	4. Turkey	295
5. France	1,694	5. France	1.833	5. Belgium	487	5. Denmark	282
6. Germany (FR)	1,473	6. Germany (FR)	1.101	6. Italy	439	6. Brazil	260
7. Poland	1.366	7. Poland	1.069	7. Romania	434	7. Indonesia	259
8. Netherland	1.213	8. United Kingdom	874	8. Germany (FR)	372	8. Germany (DR)	255
9. Italy	1.111	9. Japan	821	9. Norway	359	9. Mexico	155
10. India	1.050	10. Spain	716	10. Poland	296	10. France	139
11. Romania	854	11. Italy	672	11. Canada	291	11. United Kingdom	119
12. Canada	789	12. Germany (DR)	666	12. Kuwait	289	12. Cuba	110
13. Spain	773	13. Mexico	531	13. Bulgaria	191	13. Vietnam (South)	110
14. United Kingdom	755	14. Canada	498	14. Austria	99	14. Philippines	93
15. Belgium	652	15. Hungary	493	15. Trinidad	60	15. Sweden	85
16. Bulgaria	519	16. CSSR	448	16. Spain	57	16. Sudan	70
17. Korea (Rep.of)	447	17. Turkey	430	17. Saudi Arabia	57	17. Hungary	69
18. Norway	445	18. Brazil	425	18. Chile	47	18. Colombia	68
19. CSSR	424	19. Romania	420	19. Korea (Rep.of)	36	19. Malaysia	67
20. Hungary	424	20. Korea (Rep.of)	411	20. Finland	34	20. Thailand	62
21. Germany (DR)	411	21. Netherlands	397	21. Greece	24	21. El Salvador	61
22. Mexico	376	22. Egypt	380	22. Portugal	22	22. Peru	59
23. Yugoslavia	350	23. Yugoslavia	368	23. Australia	21	23. Morocco	55
24. Pakistan	300	24. Denmark	365	24. South Africa	16	24. Sri Lanka	51
25. Kuwait	289	25. Indonesia	350	25. Qatar	14	25. Pakistan	42

TABLE1.7(CONTINUED)

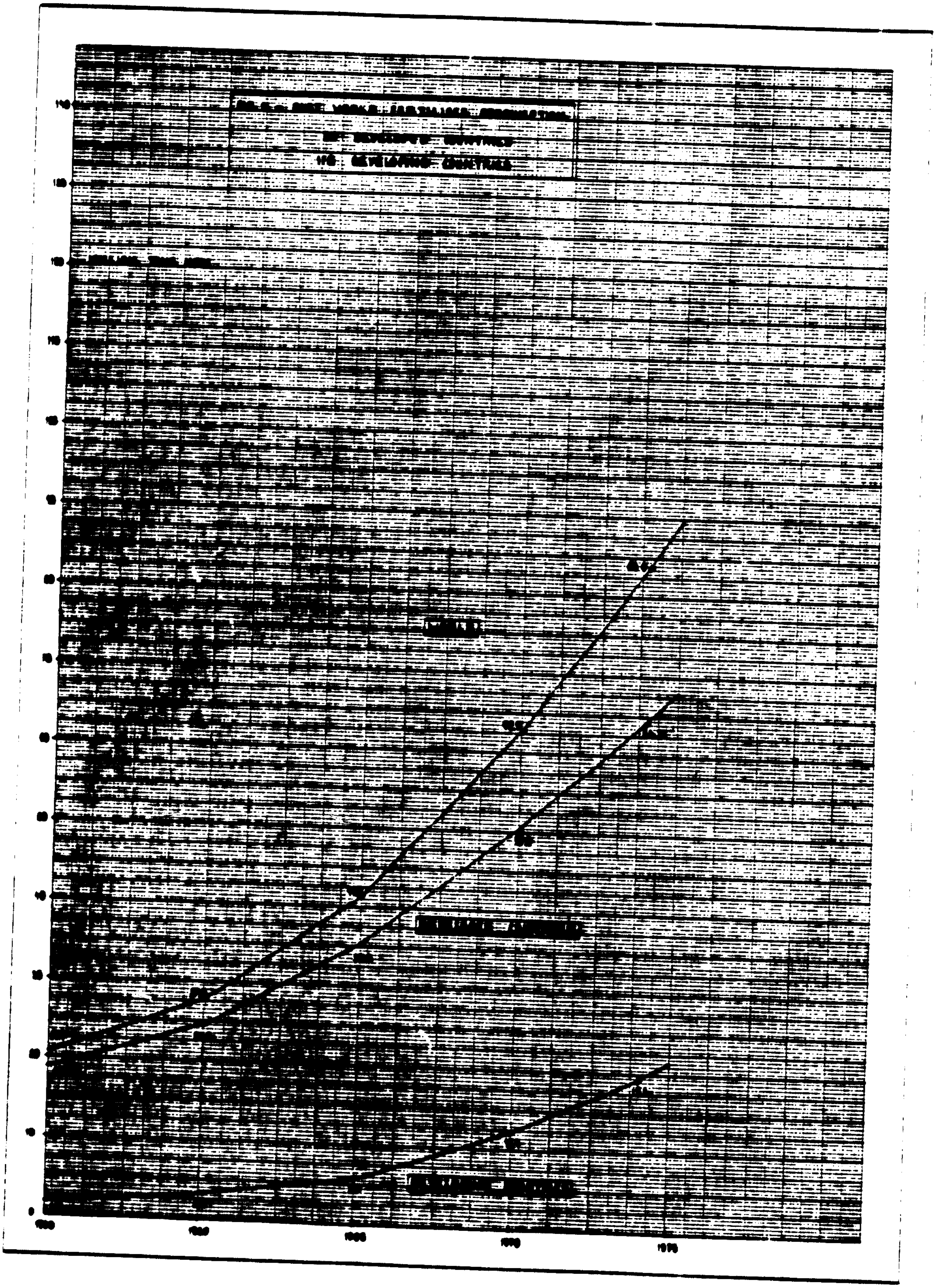
B. PHOSPHATE FERTILIZER (THOUSANDS OF TONS OF P_2O_5)

PRODUCERS		CONSUMERS		SURPLUSES		DEFICITS	
1. United States	6,013	1. United States	4,600	1. United States	1,413	1. France	454
2. USSR	3,236	2. USSR	2,699	2. USSR	537	2. Brazil	378
3. France	1,693	3. France	2.147	3. Belgium	463	3. India	309
4. China	1.314	4. China	1,390	4. Netherlands	243	4. Turkey	183
5. Australia	1.169	5. Australia	1,171	5. Canada	240	5. Hungary	127
6. Germany (FR)	962	6. Germany (FR)	917	6. Tunisia	165	6. Bulgaria	124
7. Poland	814	7. Poland	847	7. Luxembourg	132	7. Indonesia	85
8. Japan	736	8. Japan	793	8. Morocco	125	8. China	75
9. Canada	720	9. Brazil	725	9. Norway	76	9. United kingdom	61
10. Belgium	629	10. India	634	10. Yugoslavia	75	10. Japan	57
11. Spain	536	11. Spain	481	11. Mexico	74	11. CSSR	57
12. Italy	450	12. Canada	480	12. Romania	61	12. Pakistan	54
13. New Zealand	420	13. United Kingdom	478	13. Spain	55	13. Denmark	52
14. United Kingdom	417	14. Italy	476	14. Germany (FR)	45	14. Switzerland	48
15. Germany (DR)	403	15. New Zealand	445	15. Lebanon	41	15. Thailand	45
16. Romania	381	16. Germany (DR)	431	16. Austria	39	16. Bangladesh	44
17. Netherlands	350	17. CSSR	393	17. Greece	21	17. Iran	40
18. Brazil	347	18. South Africa	327	18. South Africa	21	18. Cuba	40
19. South Africa	346	19. Hungary	322	19. Sweden	15	19. Korea (Rep.of)	37
20. CSSR	336	20. Romania	320	20. Senegal	13	20. Ireland	35
21. India	325	21. Turkey	280	21. Portugal	12	21. Vietnam (South)	34
22. Yugoslavia	268	22. Bulgaria	259	22. Egypt	6	22. Poland	34
23. Mexico	255	23. Finland	197	23. Finland	4	23. Germany (DR)	28
24. Finland	202	24. Korea (Rep.of)	196	24. Tanzania	3	24. El Salvador	28
25. Hungary	195	25. Yugoslavia	193	25. Israel	2	25. Italy	26

TABLE I.X(CONTINUED)

C. POTASH FERTILIZER (THOUSANDS OF TONS OF K_2O)

PRODUCERS		CONSUMERS		SURPLUSES		DEFICITS	
1. USSR	5,918	1. United States	4,614	1. Canada	4,868	1. United States	2,268
2. Canada	5,073	2. USSR	3,605	2. USSR	2,313	2. Poland	1,413
3. Germany (DR)	2,556	3. France	1,833	3. Germany (DR)	1,898	3. Japan	685
4. Germany (FR)	2,539	4. Poland	1,413	4. Germany (FR)	1,376	4. CSSR	576
5. United States	2,346	5. Germany (FR)	1,163	5. Israel	515	5. Brazil	523
6. France	2,082	6. Japan	685	6. Congo	259	6. United Kingdom	493
7. Israel	515	7. Germany (DR)	658	7. France	250	7. Hungary	387
8. Spain	473	8. CSSR	576	8. Spain	208	8. India	314
9. China	300	9. China	528	9. Chile	5	9. China	228
10. Congo	300	10. Brazil	523			10. Danemark	216
11. Italy	137	11. United Kingdom	498			11. Belgium	193
12. Chile	19	12. Hungary	387			12. Ireland	181
13. United Kingdom	5	13. India	314			13. New Zealand	180
		14. Italy	268			14. Yugoslavia	174
		15. Spain	265			15. Austria	159
		16. Denmark	216			16. Finland	159
		17. Canada	205			17. Korea (Rep.of)	150
		18. Belgium	193			18. Sweden	144
		19. Ireland	181			19. Italy	130
		20. New Zealand	180			20. South Africa	126
		21. Yugoslavia	173			21. Netherlands	114
		22. Finland	159			22. Malaysia	112
		23. Austria	159			23. Australia	104
		24. Korea (Rep.of)	150			24. Cuba	97
		25. Sweden	144			25. Norway	70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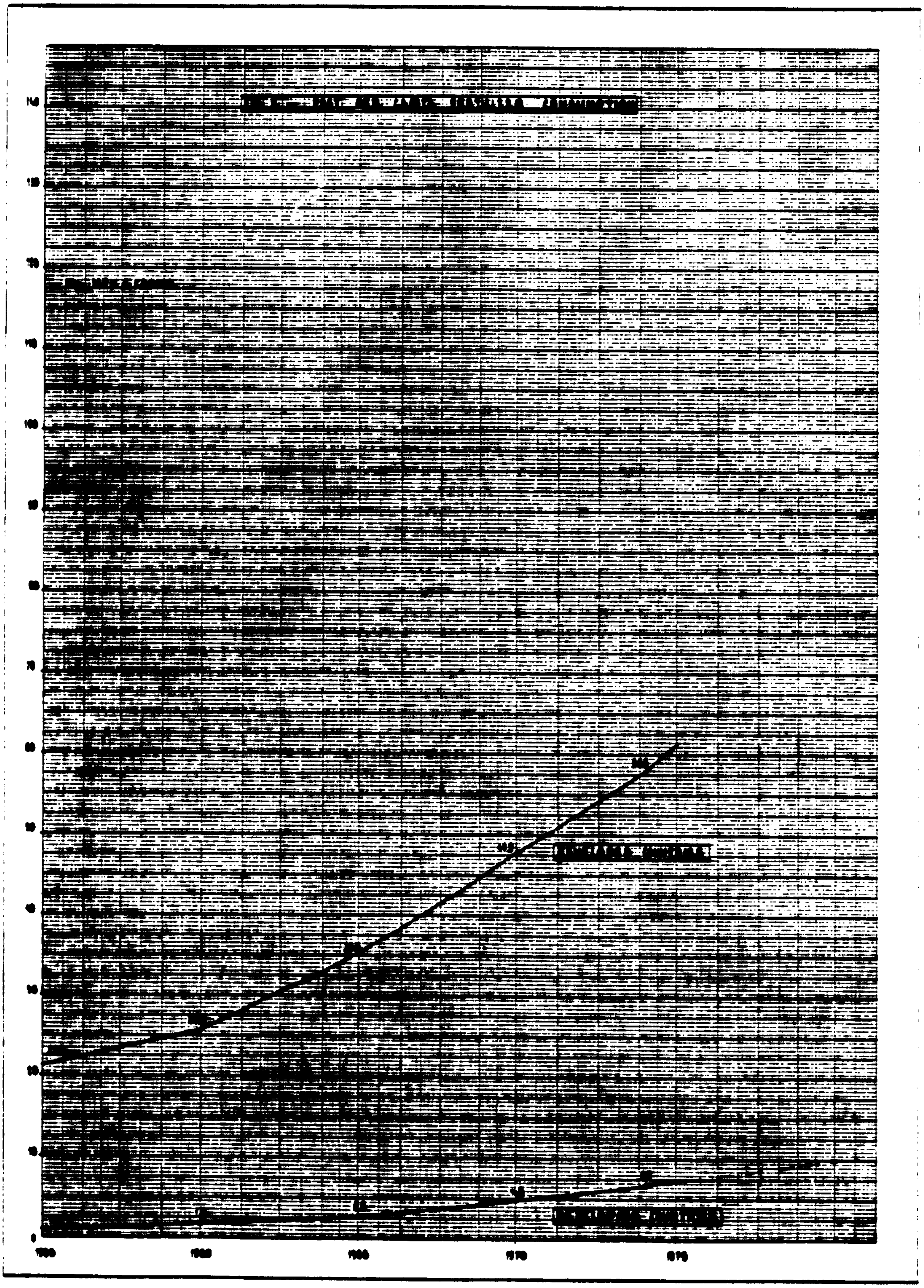
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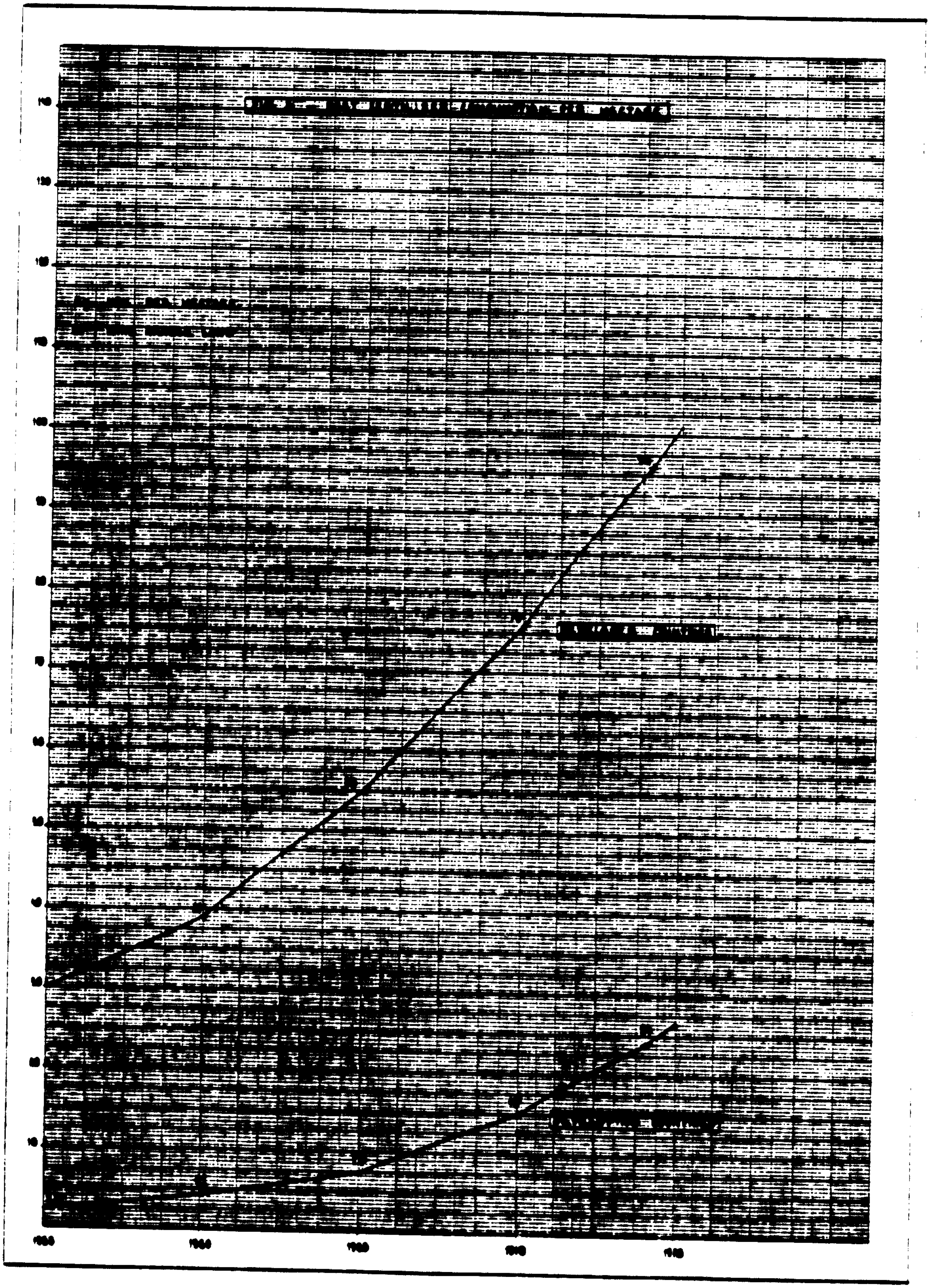

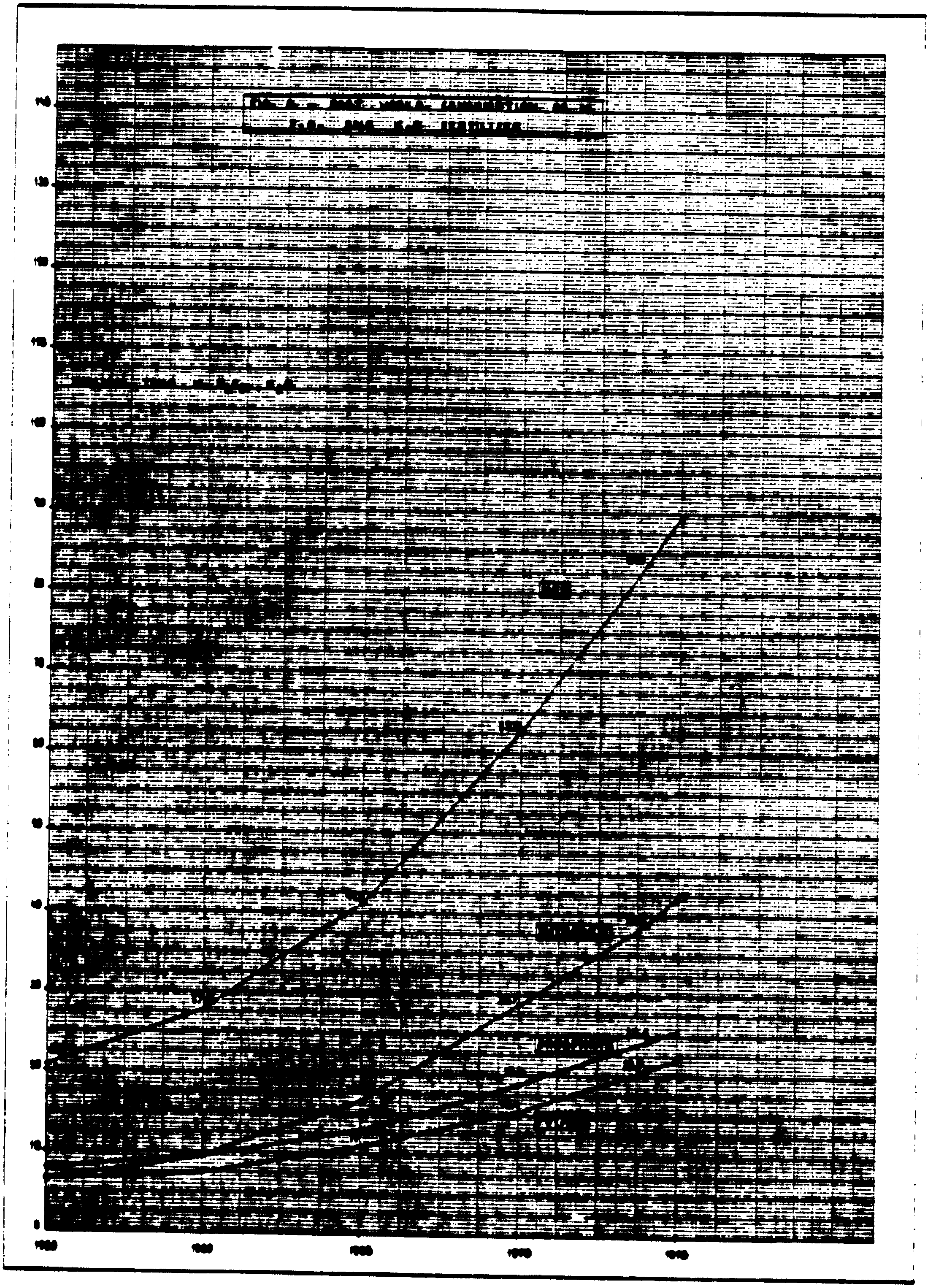
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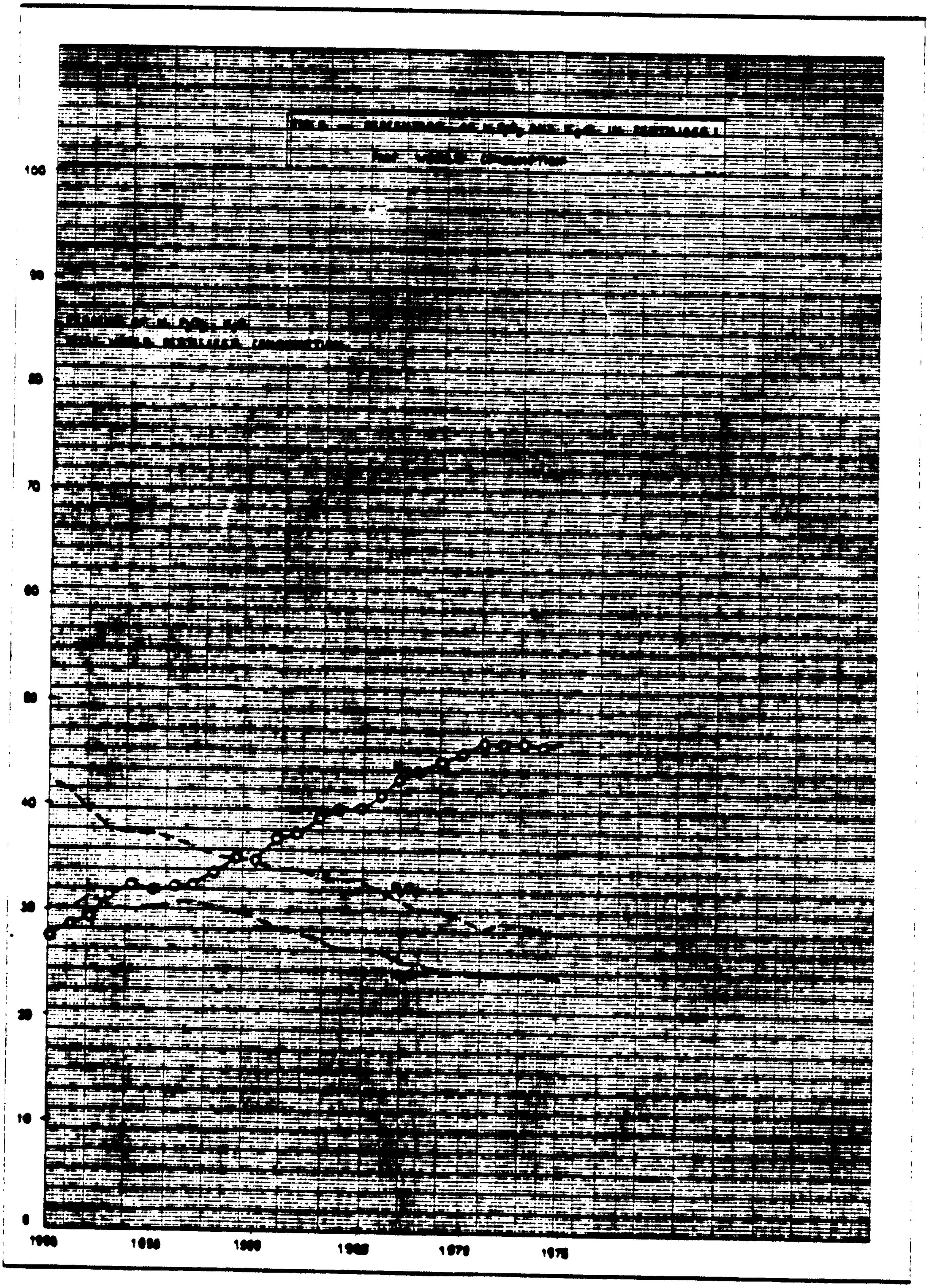
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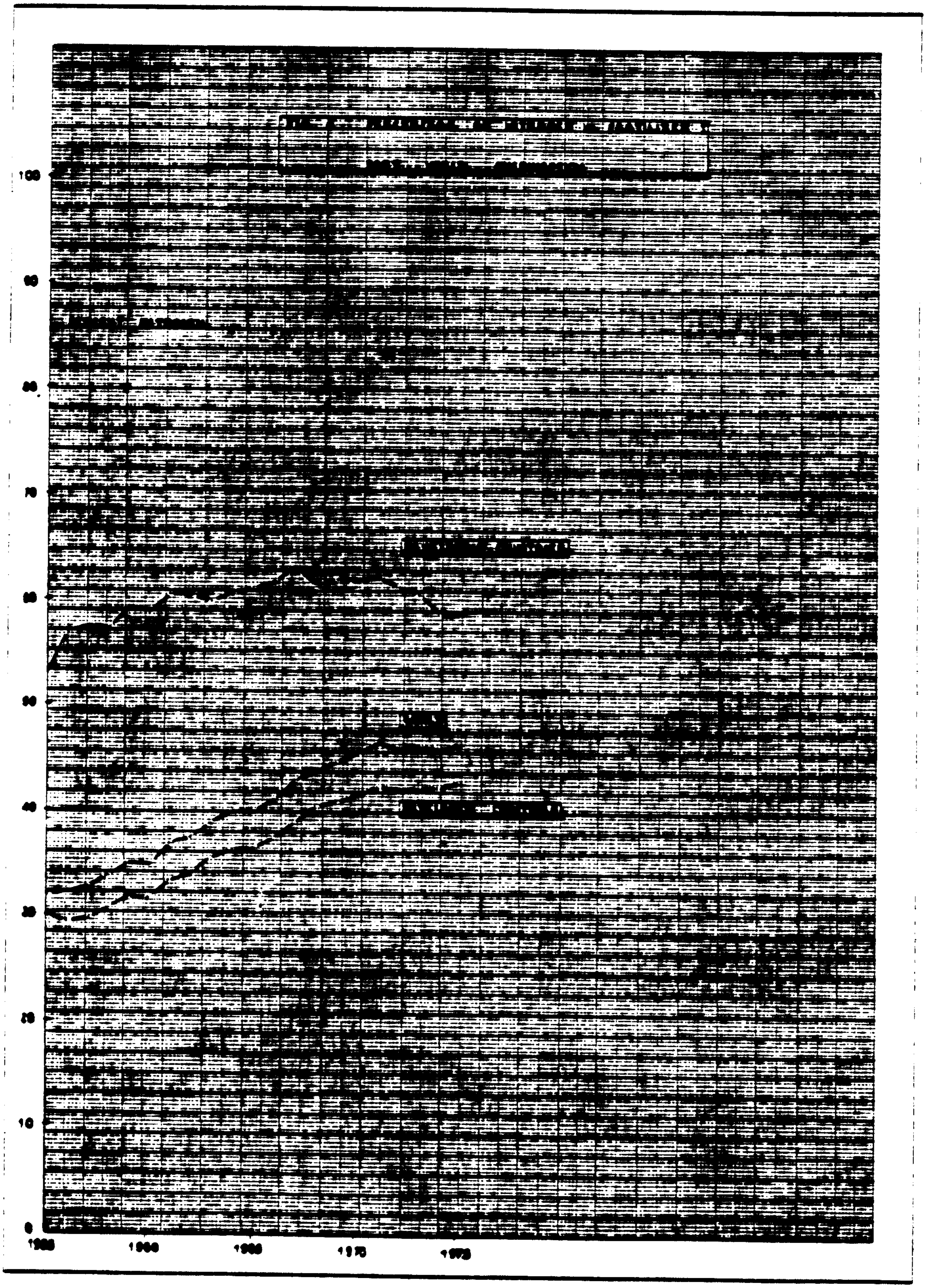
90
80
70
60
50
40
30
20
10
0
1950
1955
1960
1965
1970
1975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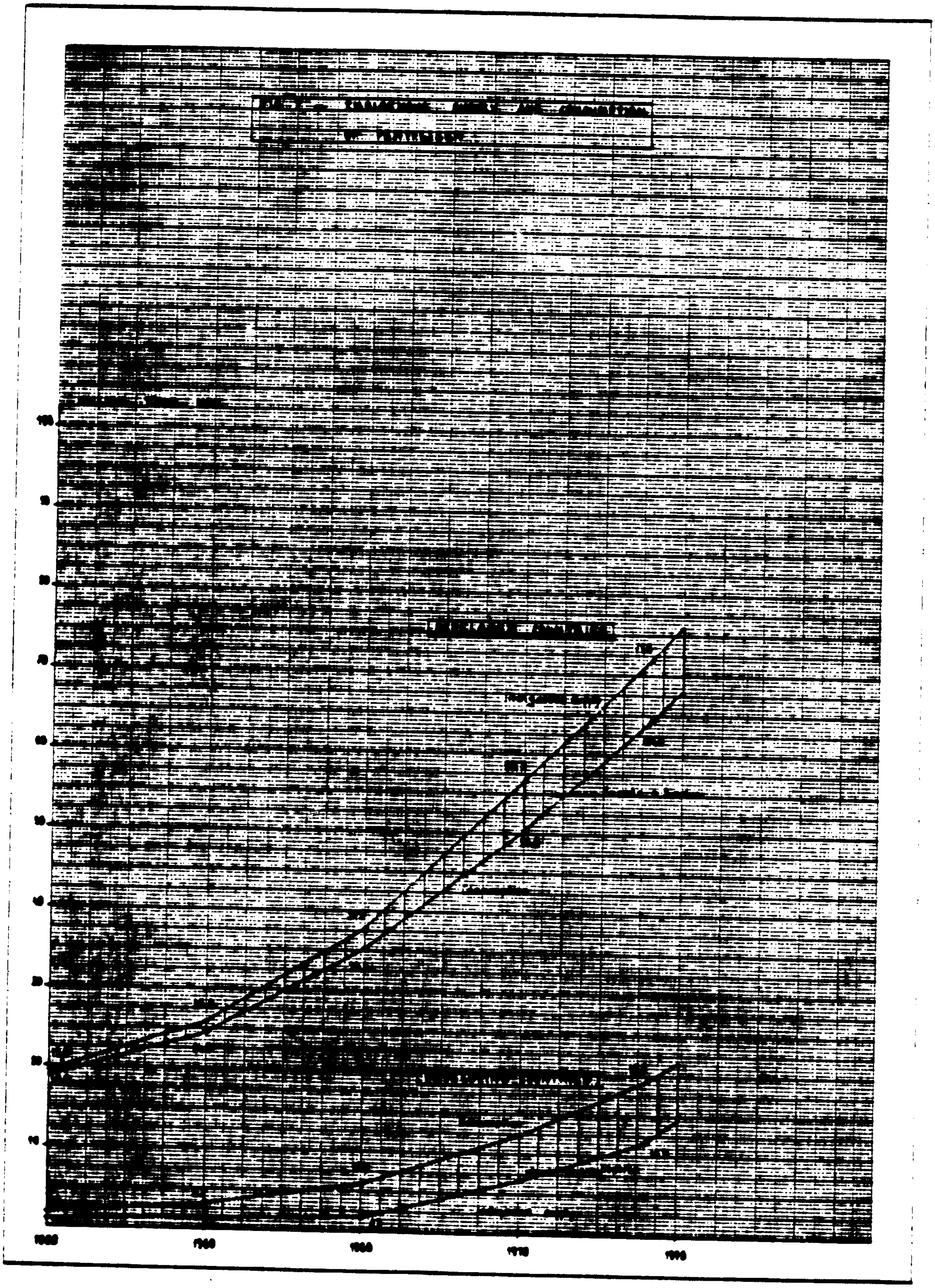
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2. FERTILIZERS DEMAND IN VIETNAM

1. Data supplied by PETROVIETNAM
2. The present situation and forecasts
3. Production programmes planned by PETROVIETNAM
4. Suitable fertilizers for VIETNAM

1. DATA SUPPLIED BY PETROVIETNAM

There is a heavy demand for fertilizers, such that the output of the complex will be able to meet only part of the total domestic demand.

Land area presently cultivated :

. Rice	5,800,000	hectares
. Others	1,500,000	hectares
Total cereals	7,300,000	hectares.

Plan objectives for 1980 :

. Rice	6,600,000	hectares
. Other cereals	2,500,000	hectares
. Industrial crops	1,400,000	hectares
. Other crops	100,000	hectares
. Market gardening	530,000	hectares
. Area to be cleared	1,000,000	hectares
. Forest area	1,200,000	hectares
TOTAL	13,330,000	hectares.

Fertilizer (urea) consumption averages 150 kg per hectare in the case of rice.

Demand can be expected to reach 2,000,000 tons by 1980, excluding fertilizer for forestry development.

2. THE PRESENT SITUATION AND FORECASTS

No data was supplied on past consumption figures, soil types, farming habits, production units, storage and blending centres or distribution systems. In view of this the market survey cannot be based on recent trends.

Some data is, however, available on South VIETNAM up to 1972/1973. In addition, the FAO have some details of nitrogen fertilizer consumption in VIETNAM. These are shown in the tables which follow.

Table 2.1 gives nitrogen consumption figures for VIETNAM as a whole. Some variations appear between the figures in the previous table and the second table, and these may be partly explained by end-of-year stocks, which may vary considerably from one year to another.

Another important factor to be taken into account in forecasting fertilizer consumption is the area of cultivated land (table 2.3.).

The most important crop is thus rice, but consumption per hectare varies according to the type of rice, harvests and the region itself.

Taking the consumption figure given by PETROVIETNAM, i.e. 150 kg of urea on average per hectare of rice, present rice crops must require 870,000 tons of urea ; by 1980 - at the same rate - consumption should reach 1,000,000 tons. To these figures must be added the phosphoric, potassic and nitrogen fertilizers required for other crops.

On the basis of 1980 cultivated land and consumption Plan objectives, consumption per hectare would be 180 kg of fertilizer as finished product, equivalent to about 72 kg of NPK.

The 1974 "FAO production year book" shows average consumption in VIETNAM as being 42 kg NPK. Without being totally unrealistic it seems difficult to meet the 1980 objective, especially in view of the foreign currency expenditure necessary.

TABLE 2.1

NUTRIENT CONSUMPTION IN SOUTH VIETNAM

IMPORTS - 1,000 TONS

	NITROGEN	P2O5	K2O	TOTAL
1963	59	37	11	107
1964	33	41	8	82
1965	26	57	11	94
1966	66	35	13	114
1967	60	21	25	106
1968	25	4	1	30
1969	140	52	25	217
1970	137	62	25	224
1971	59	15	6	80
1972	96	31	18	145
1973	132	40	24	196

TABLE 2.2.

NITROGEN FERTILIZER CONSUMPTION IN VIETNAM

	1971	1972	1973	1974	1975	1976
TOTAL NITROGEN of which	129	120	114	135	190	241
NORTH	31	13	21	46	100	
SOUTH	98	107	93	89	90	

TABLE 2.3.

CULTIVATED LAND (HECTARES)

	SOUTH	NORTH	PRESENT	PLAN OBJECTIVE 1980
RICE	2700	2200	5800	8600
SWEET POTATO	38	198		
CASSAVA	32	110		
MAIZE	36	200		
GROUND NUTS	35	50		
RUBBER	83			
BEANS		60		
OTHER	225	113		

These figures were obtained from UN statistics.

3. PRODUCTION PROGRAMMES PLANNED BY PETROVIETNAM

PETROVIETNAM have put forward three possible alternatives :

- <u>Alternative 1</u>

Ammonia	1,000 t/day
Urea	200,000 t/yr
Nitrophosphates 20/30	300,000 t/yr
Ammonium nitrate	300,000 t/yr
Nitric acid	10,000 t/yr

- <u>Alternative 2</u>

Ammonia	1,000 t/day
Urea	500,000 t/yr
Ammonium nitrate	150,000 t/yr
Nitric acid	10,000 t/yr

- <u>Alternative 3</u>

Ammonia	1,000 t/yr
Urea	575,000 t/yr

4. SUITABLE FERTILIZER FOR VIETNAM

It is difficult to make a detailed study of the types of fertilizer best suited to VIETNAM on account of the lack of data on crop and soil types. However, as the principal crop is clearly rice, various points can be considered :

For rice growing nitrogen in ammoniacal form gives better all-round results than nitrogen in nitrate form.

The nitrate ions, being mobile, are more rapidly leached and are also subject to denitrification, i.e. N_2O or N reduction, facilitated by the absence of air as is the case with irrigate crops.

Nitrate nitrogen is therefore not recommended for basic manuring.

In addition, nitrites formed during nitrate reduction may be harmful to the plant.

These drawbacks may be minimised, however, by applying the fertilizer in several successive doses, particularly during the final growth stage to promote ripening of the grain.

Phosphourous in P_2O_5 form should be applied at the start of growth in order to promote development of a good root system.

The form in which phosphorous should be applied depends upon soil type. In non-acid soil phosphorous should be used in soluble form whereas in acid soil dicalcium phosphate will give the same if not better results.

Taking the different fertilizers proposed in the three alternatives, it can be seen that urea, with 100 % ammoniacal nitrogen, is entirely suited to rice crops, while ammonium nitrate with 50 % ammoniacal and 50 % nitrate nitrogen can be used only in fairly small quantities and is thus less suitable for rice ; finally, 20-30 nitrophosphate with 65-70 % ammoniacal nitrogen is a relatively satisfactory type of fertilizer for rice as in addition to nitrogen it gives phosphorous, necessary for growth. The percentage of ammoniacal nitrogen varies according to the nitrophosphate formula, i.e. a 20-20 fertilizer has a less favourable ammoniacal nitrogen ratio - around 55 %.

3. CHOICE OF RAW MATERIAL

1. Introduction
2. Comparison of processes of naphtha steam reforming and fuel partial oxidation for ammonia production
3. Utility production
4. Economic study

1. INTRODUCTION

Inudstrially ammonia is produced by reacting hydrogen with nitrogen. Nitrogen is removed from the air and hydrogen is produced by various processes.

Modern plants consuming hydrogen in large quantities use hydrocarbons as raw materials, sources being natural gas, naphtha and fuel oil.

The two main processes presently used are steam reforming and partial oxidation.

Partial oxidation can normally use as feedstock all the hydrocarbons from natural gas to heavy fuel.

Steam reforming can use feedstocks ranging from natural gas to naphtha.

In the case of VIETNAM, we will only compare the production costs of ammonia, from a steam reforming of naphtha and a partial oxidation of fuel. We will suppose that in a first stage, natural gas is not available.

2. COMPARISON OF PROCESSES OF NAPHTHA STEAM REFORMING AND FUEL PARTIAL OXIDATION FOR AMMONIA PRODUCTION

2.1. AMMONIA PRODUCTION BY STEAM REFORMING OF NAPHTHA

The production unit includes the following sections :

- Hydrodesulphurization of the feedstock

  Sulphur is eliminated by a catalytic hydrodesulphurization (Mo/Co) in vapour phase, followed by an absorption of the last traces of H_2S on a zinc oxide bed.

- Steam reforming

  The tubes of the primary reforming furnace are filled up with nickel catalyst. The operating pressure is 35 bars and temperature is 900°C. On account of high temperatures of tubes in the furnace, naphtha is used for the firing. The metals contained in an average heavy fuel would lead to the formation of fusible alloys on the tube walls and their deterioration. Refinery fuel gas or low sulphur content fuel will replace naphtha economically if they are available.

  In a secondary reformer, catalytic combustion (Ni catalyst) of residual methane is operated with air which allows the introduction of nitrogen required for ammonia synthesis.

- Shift conversion of carbon monoxide

  The steam shift conversion of carbon monoxide is realized in two reactors in series.

- Carbon dioxide elimination

  It is operated in two stages :

  - a roughing by a potassium carbonate solution
  - finishing epuration with monoethanolamine part of the CO_2 recovered is used for urea production.

- Carbon monoxide elimination by methanation

  Catalytic hydrogenation allows residual content of about 10ppm to be obtained.

- Compression

  Centrifugal compressor with two stages allows synthetis gas to be compressed and recycled.

- Ammonia synthesis

  Synthesis is carried out by a "low pressure" process (40-50 bars), with a iron oxide catalyst.

  The ammonia unit is self sufficient in steam.

2.2. AMMONIA PRODUCTION BY FUEL PARTIAL OXIDATION

The production unit has the following sections :

- Air fractionation

  Fractionation is obtained by distillation of the liquid air at low remperature. The unit produces nitrogen required for ammonia synthesis.

- Partial oxidation of fuel

  The oxidation of fuel is realised by oxygen without catalyst, with a pressure of 85 bars (high pressure process). The temperature is close to 1400°C. Effluent leaving the furnace is subjected to a rapid water quench in order to stop the oxidation.

- Recovery of the soot

  Quench waters containing soot are filtrated ; soot is recovered and used in boiler burners.

- Shift conversion of carbon monoxide

  The steam shift conversion is carried out in a reactor containing a sulphur resisting catalyst.

- Elimination of carbon dioxide and of H_2S

  This elimination is carried out by washing with triethanol amine. Part of the recovered CO_2 is used for urea production.

- Carbon monoxide elimination

  Washing with liquid nitrogen from the air fractionation removes the last traces of CO.

- Ammonia synthesis

  Synthesis is carried out on an iron oxide catalyst. The recycled gas is compressed by a centrifugal compressor The ammonia unit is self sufficient in steam and electricity.

3. UTILITY PRODUCTION

STEAM AND ELECTRICITY

1. For the steam reforming of naphtha, an auxiliary boiler is planned in the plant in order to produce the quantities of steam required for the start up and normal operation of the plant.

   The steam produced in the recovery boilers is superheated in the convection zone of the reforming furnace, then mixed with the superheated steam produced in the auxiliary boiler in order to drive the steam turbines of centrifugal compressors (synthesis gas, air, ammonia) and certain boiler water pumps.

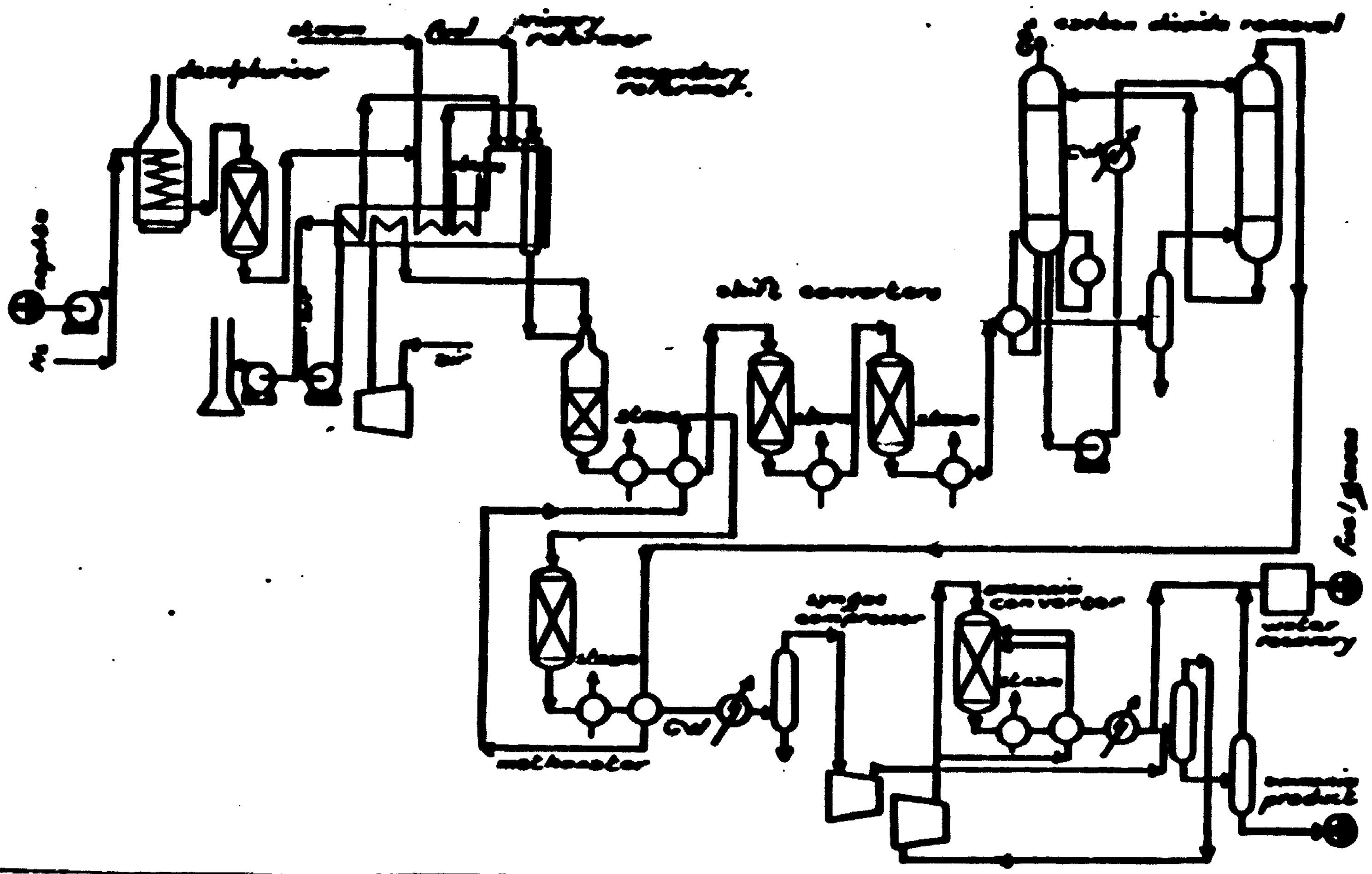
   A turbogenerator is integrated into the ammonia plant. It is driven by a steam turbine fed by an auxiliary boiler.

2. For the partial oxidation, a central boiler produces hp steam which is used to drive four centrifugal compressors of the unit, air, nitrogen, synthesis gas and ammonia.

   A turboalternator is planned inside the ammonia plant ; it is driven by steam furnished by the central boiler.

CONSUMPTION PER TON OF AMMONIA

	Steam reforming of naphtha	Partial oxidation of fuel
Naphtha process 10^6 kcal LHV	5.46	
Fuel Low sulphur content (fuel) 10^6 kcal LHV	3.83	
Fuel oil (Process + fuel) 10^6 kcal LHV		9.12
Cooling water $\Delta T = 10°C$ m^3	400	425
Demineralized water m^3	1.3	1.3


naphtha
N_2
desulphuriser
steam
fuel
primary reformer
secondary reformer.
air
shift converters
steam
steam
steam
CO_2
carbon dioxide removal
CW
fuel/gases
methanator
steam
CW
syngas compressor
ammonia converter
steam
water recovery
ammonia product

4. ECONOMIC STUDY

4.1. INTRODUCTION

The bases of the economic calculation are generally the same as those used for refining (see volume III).

The overall installed cost budget ratio between WESTERN EUROPE and VIETNAM for an ammonia plant is presented in the following table 3.1.

For the working capital, we will take only one month of final products.

The utilities costs are as follows :

. industrial water	5¢/m^3
. fuel	8.7 US$/$10^6$kcal

The local prices of naphtha, low sulphur content fuel, fuel with 3.5 % sulphur weight have been defined in the refinery study.

. Naphtha	156 US$/ton
. Fuel LSC	90 US$/ton
. Fuel 3.5 % S	87 US$/ton

At this stage of the project, a simple economic evaluation of the two alternatives will be carried out.

We will calculate successively on a yearly basis :

I	Investment cost
D	Depreciation
O	Operating cost
S	Sales revenue
R	Raw materials cost

Production cost $P = O + R$

Gross cash flow $GCF = S - P$

Tax base $GCF - D$

Tax $T = (GCF-D) \times 0.4$

After tax cash flow $ATCF = CGF - T$

Reimbursement period before taxes (in years) $\frac{I}{GCF}$

Reimbursement period after taxes (in years) $\frac{I}{ATCF}$

AMMONIA PRICE

The ammonia price taken in the study is 213 US$/ton, 20 % to 30 % higher than average prices in EUROPE.

TABLE 3.1.

OVERALL INSTALLED COST BUDGET RATIO

	WESTERN EUROPE	RATIO	VIETNAM
CALCULATED COST			
• Material	100	1.1	110
• Transport to site	5		15
SUB TOTAL 1	105		125
• Home office services	20	1.1	22
SUB TOTAL 2	20		22
• Construction works			
- Field engineering supervision	12	2	24
- Civil works	28	1.2	33
- Erection works	40	1.7	68
SUB TOTAL 3	80		125
• Start-up supervision	5	3	15
TOTAL TECHNICAL COST	210	1.37	287
Installed cost budget factors on the calculated cost			
• Provision for contingency	1.15		1.25
INSTALLED COST BUDGET	241	1.49	358

4.2. INVESTMENTS

The costs are given in mid 1978 US$. (see table 3.2.).

TABLE 3.2.

INVESTMENTS

IN 10^3US$

	PARTIAL OXYDATION	STEAM REFORMING OF NAPHTHA
PROCESS UNITS	92 000	69 000
OFFSITES - UTILITIES	46 000	34 500
ERECTED COST IN EUROPE	138 000	103 500
TOTAL COST IN EUROPE	158 700	119 025
TOTAL COST IN VIETNAM	236 480	177 350
SPARE PARTS	8 240	5 180
CATALYSTS AND CHEMICALS	450	900
ROYALTIES	2 500	2 500
PRE OPERATING EXPENSES and START-UP EXPENSES	16 550	12 420
TOTAL INVESTMENT EXCLUDING FINANCIAL CHARGES	264 200	199 350
WORKING CAPITAL	5 700	6 700

TABLE 3.3.

CONSUMPTION OF RAW MATERIALS

	PARTIAL OXYDATION		STEAM REFORMING	
	per ton of NH_3	per year in tons	per ton of NH_3	per year in tons
NAPHTHA PROCESS	0.524	172 920		
FUEL in TONS	0.392	129 500		
FUEL OIL (Process + fuel) in TONS			0.935	308 550
INDUSTRIAL WATER	22	7 260 000	23.5	7 755 000

TABLE 3.4.

OPERATING COST

IN 10^3US$

	PARTIAL OXIDATION	STEAM REFORMING OF NAPHTHA
VARIABLE CHARGES		
• Naphtha		26 975
• Fuel low sulphur content		11 655
• Fuel	26 844	
• Industrial water	388	363
• Catalyst and chemical	420	1 200
TOTAL	27 652	40 193
FIXED CHARGES		
• Manpower	195	195
• Technical assistance	39	39
• Maintenance	4 120	3 090
• Insurance	1 585	1 195
• General overheads	70	
• Land rent	30	
• Interest on working capital	670	670
Sub total	6 709	5 290
TOTAL OPERATING COST	34 361	45 483

TABLE 3.5.

ECONOMIC COMPARISON

IN 10^3US$

	PARTIAL OXYDATION	STEAM REFORMING OF NAPHTHA
SALES	72 100	72 100
OPERATING COST	34 360	45 483
GROSS CASH FLOW	37 740	26 617
TOTAL INVESTMENT	264 200	199 350
PAY OUT TIME	7	7.49
DEPRECIATION	17 613	13 290
TAX BASE	20 128	13 327
TAX	8 050	5 330
AFTER TAX CASH FLOW	29 690	21 288
PAY OUT TIME	8.89	9.36

4.3. CONCLUSION

Profitability is thus slightly higher with fuel partial oxydation than with naphtha steam reforming, though the difference is not very great. In fact if naphtha were 10 % cheaper, payout periods would be the same.

Further, if the two methods gave the same profitability, the price ratio of fuel to naphtha would be 0.6.

Taking international prices for these two feedstocks, i.e. 70 US$/ton for fuel and 140 US$/ton for naphtha, payout times for the two methods are improved, viz. 6.78 instead of 7.3 years for steam reforming and 6.19 instead of 7 years in the case of partial oxydation.

Variations in payout times according to feedstock prices are shown in the figure which follows.

In choosing between these two methods other criteria may also be considered, e.g. availability of raw materials, or flexibility.

From the refining study it can be seen that in the simplest refining scheme large quantities of fuel oil are available whereas if naphtha is to be obtained the refining scheme has to be much more complex and investment higher. Fuel thus seems to be more readily available than naphtha.

It can also be said that future trends in availability on the international market and in prices appear more favourable for fuel than for naphtha, i.e. surpluses of the former will be available at low prices whereas naphtha if available will be expensive.

Note also that partial oxidation can operate on a wide range of feedstocks from gas to vacuum residue, but steam reforming can operate only on gas and naphtha.

It should also be pointed out that over 3,000,000 tons of ammonia are produced in the world using partial oxidation.

For these various reasons we would be inclined at this stage in the study to opt for the fuel partial oxydation method, while not actually reaching a final decision on this yet.

In the discussion that follows the three fertilizer complexes to be compared will be based on partial oxydation for ammonia manufacture.

We must emphasize, however, that the only choice made is between fuel partial oxidation and naphtha steam reforming, because should natural gas be found and become available, the choice would be different with gas steam reforming probably being recommended. (see appendix 2)

4. ECONOMIC AND TECHNICAL STUDY OF THE THREE COMPLEXES PLANNED BY PETROVIETNAM

1. Complex urea and nitrophosphate Alternate I
2. Complex urea-ammonium nitrate Alternate II
3. Complex urea-ammonia Alternate III
4. Economic study
5. Results
6. Fertilizers shipping

1. COMPLEX : UREA AND NITROPHOSPHATE
ALTERNATE I

1.1. INTRODUCTION

Alternate I includes the following units :

. Ammonia	1,000 t/day
. Urea	200,000 t/year
. Nitrophosphates	300,000 t/year
. Ammonium nitrate	333,000 t/year
. Nitric acid	364,000 t/year, of which 10,000 tons nitric acid at 98 %

Ammonia will be produced by the partial oxidation route. All the data in this chapter, raw materials consumptions, utilities consumptions, are average data which can slightly varied according to the processes.

1.2. DESCRIPTION OF PROCESSES

Descriptions are given in the annex.

1.3. MATERIAL BALANCE OF THE COMPLEX

NITROPHOSPHATE UNIT

At this level of the study, we will take yields of a phosphate type KOLA, the composition of which is similar to the composition of a Vietnamese phosphate.

Raw material consumption		Per ton of 19.5:20:0 nitrophosphate	Per year tons
Phosphate rock	tons	0.75	225 000
Nitric acid (as 100%)	tons	1.18	354 000
Ammonia	tons	0.39	117 000
Carbon dioxide	tons	0.27	81 000
Kielselguhr	(kg)	(5-10)	1500-3000
By products			
. Ammonium nitrate	tons	1.11	333 000
. Calcium carbonate	tons	0.57	171 000

NITRIC ACID UNIT

The total yearly capacity is : 354 000 tons for nitrophosphate
10 000 tons
364 000 tons.

This capacity is an order of magnitude because the quantity of nitric acid required for Vietnamese phosphate rock could change slightly.

Raw material consumption	Per ton	Per year tons
Ammonia	0.282	103 000

UREA UNIT

The total yearly capacity is 200 000 tons.

Raw materials consumptions	Per ton	Per year
. Ammonia	0.58	115 000
. Carbon dioxide	0.77	154 000

AMMONIA UNIT

The total yearly capacity is 336 000 tons.

The total material balance of the complex can be summed up in the following table. (table 4.1.)

1.4. UTILITIES BALANCE

The utilities balance of the complex is summarized in the following table (table 4.2.).

TABLE 4.1.

TOTAL MATERIAL BALANCE - ALTERNATE I

PRODUCT	CAPACITY tons/year	NH_3	NITRIC ACID	PHOSPHATE ROCK	AMMONIUM NITRATE	$CaCO_3$	CO_2
NITROPHOSPHATE	300 000	117 000	354 000	225 000	333 000	171 000	81 000
NITRIC ACID	364 000	103 000					
UREA	200 000	116 000					154 000
TOTAL		336 000	354 000	225 000	333 000	171 000	235 000

TABLE 4.2.

UTILITIES BALANCE ALTERNATE I

PRODUCT	CAPACITY tons/year	Electricity kWh/h	Steam HP	Steam MP	Steam LP	Cooling water m³/h	Process water m³/h	Fuel 10^6 kcal/h
NITROPHOSPHATE	300 000	6 150		48.75		1 100		
NITRIC ACID	364 000	409	-7.6	4.75		6 825	18.2	
UREA	200 000	1 250		28.5	-8.5	1 750		
NH_3	336 000					17 780	54.6	383
TOTAL		7 809	-7.6	82	-8.5	27 455	72.8	383
OFFSITES		6 170				1 045	20.2	55
TOTAL		14 220	-7.6	82	-8.5	28 500	93.0	438

2. COMPLEX : UREA-AMMONIUM NITRATE - ALTERNATE II

2.1. INTRODUCTION

Alternate II includes the following units :

. Ammonia	1 000 tons/day
. Urea	450 000 tons/year
. Ammonium nitrate	150 000 tons/year
. Nitric acid	130 000 tons/year

Ammonia will be produced by the partial oxidation route. All the data in this chapter raw materials consumption, utilities consumption, are average data which can be slightly varied according to the processes.

2.2. DESCRIPTION OF PROCESSES

Description are given in the annex

2.3. MATERIAL BALANCE OF THE COMPLEX

AMMONIUM NITRATE

The total yearly capacity is 150 000 tons/year.

Raw materials consumption	Per ton	Per year tons
. Ammonia	0.217	32 550
. Nitric acid	0.800	120 000

NITRIC ACID

The total yearly capacity is 130 000 tons/year.

Raw materials consumption	Per ton	Per year tons
. Ammonia	0.282	36 600

UREA

The ammonia unit capacity being 330 000 tons/year the quantity of ammonia available for urea will be 260 738 tons, hence 450 000 tons of urea.

The total material balance of the complex can be summarized in the following table (table 4.3.).

2.4. UTILITIES BALANCE

The utility balance of the complex is summarized in the following table (table 4.4.).

TABLE 4.3.

TOTAL MATERIAL BALANCE

ALTERNATE II

PRODUCT	CAPACITY tons/year	NH_3	NITRIC ACID	CO_2
AMMONIUM NITRATE	150 000	32 550	120 000	
NITRIC ACID	130 000	36 380		
UREA	450 000	261 000		348 500
TOTAL		330 210	120 000	348 500

TABLE 4.9.

TOTAL UTILITIES BALANCE

ALTERNATE II

PRODUCT	CAPACITY tons/year	ELECTIRICTY kWh/h	STEAM HP	STEAM MP	STEAM LP	COOLING WATER m^3/h	PROCESS WATER m^3/h	FUEL 10^6kcal/h
AMMONIUM NITRATE	150 000	260		2.5	1.7	560		
NITRIC ACID	130 000	145	-2.7	1.7		2 440	6.5	
UREA	450 000	555		12.7	-3.9	780		
AMMONIA	331 000					17 780	54.6	383
TOTAL		960	-2.7	17	-2.1	21 560	61.1	383
OFFSITES		5 085				1 040	19.9	11
TOTAL		6 045	-2.7	17	-2.1	22 600	81.0	394

3. COMPLEX UREA-AMMONIA - ALTERNATE III

3.1. INTRODUCTION

Alternate III includes the following units.

.	Ammonia	1 000 tons/day
.	Urea	570 000 tons/year.

Ammonia will be produced by the partial oxidation route. All the data in this chapter, raw materials consumption, utilities consumption, are average data which can be slightly varied according to the processes.

3.2. DESCRIPTION OF PROCESSES

Descriptions are given in the annex.

3.3. MATERIAL BALANCE

The material balance of the urea unit is the following :

Raw material consumption	Per ton	Per year
· Ammonia	0.58	331 000
· CO_2	0.77	439 000

3.4. UTILITIES BALANCE

The utility balance is summarized in the following table (table 4.5.).

TABLE 4.5.

TOTAL UTILITIES BALANCE ALTERNATE III

PRODUCT	CAPACITY tons/year	ELECTRICITY kWh/h	STEAM HP	STEAM MP	STEAM LP	COOLING WATER m^3/h	PROCESS WATER m^3/h	FUEL 10^6kcal/h
UREA	570 000	703		16.1	-4.8	980		
AMMONIA	331 000					17 780		383
TOTAL		703		16.1	-4.8	18 760	54.6	383
OFFSITES		4 387				732	18.4	8
TOTAL		5 090		16.1	-4.8	19 500	73	391

4. ECONOMIC STUDY

4.1. INTRODUCTION

The bases of the economic calculation are generally the same as those used for refining (see volume III).

The overall installed cost budget ratio between WESTERN EUROPE and VIETNAM for a fertilizer complex was presented in chapter 3.

For the working capital, we will take one month of final products.

4.2. OPERATING COSTS AND OTHER COSTS

Utilities costs are as follows :

. Industrial water	5¢/m^3
. Electricity	3¢/kWh
. Fuel	3.7 US$/10^{6}kcal

The other items, such as manpower costs, supervision, maintenance, insurance, general overheads are calculated in the same way as for refining.

4.3. RAW MATERIAL COSTS

The local prices of naphtha, fuel LSC, fuel 3.5 % wt S have been defined in the refining study :

. Naphtha	156$/ton
. Fuel LSC	90$/ton
. Fuel 3.5% wtS	87$/ton

The phosphate rock price depends on the tricalcic phosphate content ; an average price of 35$/ton will be used.

4.4. PRODUCT PRICES

Product prices are generally 30 % higher than the average prices in developed countries.

. Urea	185 US$/ton
. Ammonium nitrate	140 US$/ton
. Nitrophosphate 20-30	155 US$/ton

4.5. ECONOMIC STUDY

At the level of the project, a simple economic evaluation of the three alternatives will be made.

We will calculate successively on a yearly basis

I	Investment cost
D	Depreciation
O	Operating cost
S	Sales revenue
R	Raw material costs

Production cost $P = O + R$

Gross cash flow $GCF = S - P$

Tax base $GCF - D$

Taxes $T = (GCF-D) \times 0.4$

After tax cash flow $ATCF = GCF - T$

Reimbursement period before taxes $\frac{I}{GCF}$

Reimbursement period after taxes $\frac{I}{ATCF}$

4.6. INVESTMENTS

The costs are given in mid 1978 US$ in table 4.6.

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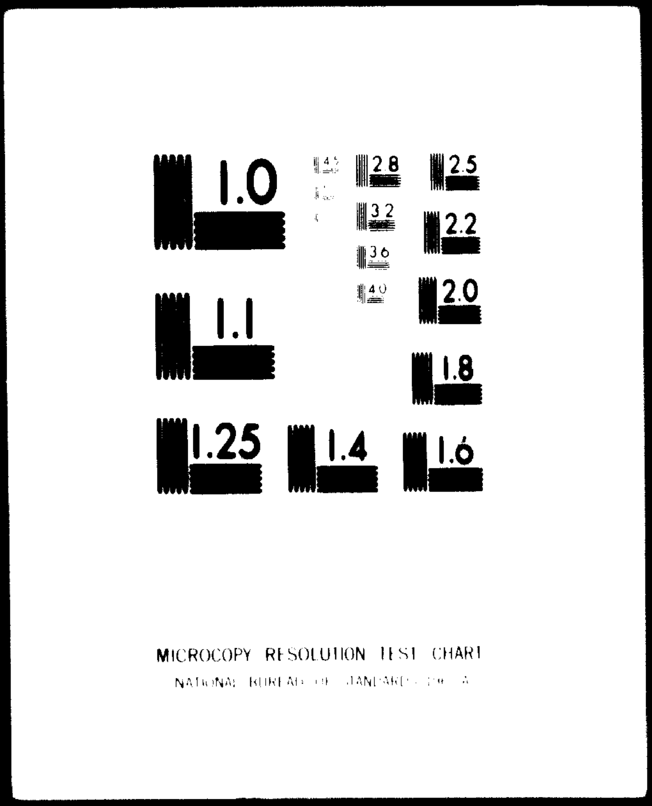

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

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TABLE 4.6.

INVESTMENTS

IN 10^3US$

	ALTERNATIVE I	ALTERNATIVE II	ALTERNATIVE III
PROCESS UNITS			
• Ammonia	92 000	92 000	92 000
• Nitric acid	20 000	10 000	
• Nitrophosphates -AN	40 000		
• Ammonium nitrate		10 000	
• Urea	17 000	29 800	32 000
TOTAL BATTERY LIMITS	169 000	141 800	124 000
OFFSITES	125 000	103 400	90 000
ERECTED COST IN EUROPE	294 000	245 000	214 000
TOTAL COST IN EUROPE	338 100	281 750	246 100
TOTAL COST IN VIETNAM	503 770	419 807	366 689
Spare parts	17 553	10 848	12 776
Catalysts and chemicals	1 650	900	450
Royalties	4 500	4 800	4 500
Pre-operating expenses and start up expenses	35 285	29 386	25 668
TOTAL INVESTMENT excluding financial charges	583 000	485 000	410 000
WORKING CAPITAL	12 400	9 900	9 900

TABLE 4.7

OPERATING COSTS

IN 10^3US$

	ALTERNATIVE I	ALTERNATIVE II	ALTERNATIVE III
VARIABLE CHARGES			
• Raw materials • Fuel	34 940	27 420	27 210
• Industrial water	607	484	397
• Electricity	3 413	1 450	1 221
• Catalysts and chemicals	1 100	2 010	1 300
Sub total	40 060	31 364	30 128
FIXED CHARGES			
• Manpower	1 100	1 000	880
• Technical assistance	220	200	178
• Maintenance	8 780	5 425	6 390
• Insurance	3 380	2 790	2 480
• General overheads	400	360	320
• Land rent	30	30	30
• Interest on working capital	1 240	990	990
Sub total	15 150	10 845	11 247
TOTAL	55 210	42 160	41 375

TABLE 4.7

ECONOMIC COMPARAISON

	ALTERNATIVE I	ALTERNATIVE II	ALTERNATIVE III
SALES	131 620	105 750	105 450
OPERATING COST	55 210	42 160	41 375
GROSS CASH FLOW	76 410	63 590	64 075
TOTAL INVESTMENT	563 000	465 000	410 000
PAYOUT TIME	7.37	7.31	6.40
DEPRECIATION	37 530	31 000	27 330
TAX BASE	38 880	32 590	36 745
TAX	15 550	13 040	14 700
AFTER TAX CASH FLOW	60 860	50 550	49 375
PAYOUT TIME	9.25	9.20	8.30

5. RESULTS

1. TECHNICAL

- The first alternative produces both nitrogenous and phosphatic fertilizers from phosphate rock available in VIETNAM. It meets the rice crop needs rather well particularly because of the high nitrogen ammonia content of urea and nitrophosphates. Ammonium nitrate production which is more convenient for dry crops - due to its high nitrogen nitrate content - is to be carefully looked at with a view to hinterland crops requirements.

- Alternatives II and III deal only with ammonia derivatives such as urea and ammonium nitrate. Alternate II which produces large amount of ammonium nitrate seems less suitable for rice than the other two. Alternate III produces only urea. While appropriate for rice crops this alternative does not supply all the fertilizer needs of such crops - no phosphatic fertilizers.

It appears that a better appraisal for the selection of one of these alternatives, whatever the economics are should result from an in-depth analysis of Vietnamese requirements, particularly rice crops.

2. ECONOMIC

Economic results of the three alternatives proposed by PETROVIETNAM can be compared from two main view points :

Investment required in VIETNAM is fairly high :

. Alternative I	563 million US dollars
. Alternative II	465 million US dollars
. Alternative III	410 million US dollars

or taking investment for Alternative III to be equivalent to 100

. Alternative I	137
. Alternative II	113
. Alternative III	100

financial charges such as insurance expenses, bank fees, interim interests are not included.

Profitabilities expressed as pay out time are not significantly different but profitability is higher in Alternative III.

Considering these both aspects only, alternative III, producing only urea, appears as the most interesting one for VIETNAM.

6. FERTILIZERS SHIPPING

Total fertilizer demand in VIETNAM is such that the complex will not fully cover requirements. Allowance will thus be made for the North being supplied in priority.

Whatever the manufacturing programme, means of shipping will be as follows :

to HANOI and NAM DINH	500 ton max. barges
to HAIPHONG and DANANG	3000 ton max. ships
to THANH HOA and VINH	road/rail.

Quantities vary according to the manufacturing programme :

	ALTERNATIVE 1	ALTERNATIVE 2	ALTERNATIVE 3
HANOI	260 000	200 000	180 000
NAM DINH	100 000	70 000	70 000
HAI PHONG	160 000	100 000	100 000
DA NANG	100 000	70 000	70 000
THANH HOA/VINH	210 000	160 000	150 000
TOTAL	830 000	600 000	570 000

Means of shipping will be

Barges (500 t)	10	9	8
Ship (3000 t)	1	1	1
Barge loading berths	2	2	2
Ship loading berth	1	1	1

PHOSPHATE ORE DELIVERY

Loading berth occupancy times are sufficiently short in the case of 3,000 t vessels as to allow 3,000 t phosphate ore carriers to use the same berth for unloading, if nitrophosphates are to be manufactured. The number of vessels used will depend on the distance to be covered.

FERTILIZER TRANSPORT FROM PLANT TO HARBOUR

As most of the output is to be shipped be sea, means of transport up to the loading quay require to be studied.

Two solutions are possible ; the final choice cannot be made until a later stage when layout and the manufacturing programme are established.

1. A conveyor belt taking the finished product in bulk form to the harbour where the bagging plant is situated, close to the loading berths. Bags will then be held in storage until dispatch.

   This solution involves only one storage unit (at the harbour), but the railway line will have to be extended as far as the quay for rail shipment. The railway can, however, be assumed to serve the harbour in any case.

2. The product is bagged at the plant and subsequently taken by lorry to the harbour where it is stored while awaiting dispatch, or possibly loaded directly if barges are being used. This solution involves additional storage capacity at the bagging plant.

A preliminary economic comparison shows that the choice between these two alternatives is governed chiefly by transport distances between plant and harbour.

Solution 2 requires low investment initially, but the frequent replacement of tractors and the high cost of maintenance point to solution 1 being preferable if the distance is under 2 km.

Table 4.8 gives a preliminary estimate of operating costs -with two alternative layouts (base n°1 and 2)- of the two means of transport, assuming urea alone to be produced.

TABLE 4.8

	LAYOUT 1		LAYOUT 2	
	Conveyor belt	Lorry	Conveyor belt	Lorry
Distance PLANT-HARBOUR	4.2	5	1.5	2
Rotation period		32		14
Daily lorry transport capacity		300		685
Number of tractors		4+1		2+1
Number of trailers		8+2		8+2
Investment	10 150 000	400 000	4 000 000	260 000
Operating costs	165 000	275 000	110 000	30 000
Amortization	508 000	170 000	200 000	108 000
TOTAL	673 000	445 000	310 000	338 000

PHOSPHATE TRANSPORT FROM HARBOUR TO FERTILIZER PLANT

If nitrophosphates are to be produced, bulk phosphate can be economically transported to the fertilizer plant by conveyor belt, especially if the plant is near the harbour.

Cost estimates and economic comparisons made in the previous paragraph can as an initial approximation be applied to phosphate delivery also.

ANNEXE 1

DESCRIPTION OF PROCESSES

A. Partial oxidation of fuel for ammonia production

B. Urea production

C. Nitric acid production

D. Ammonium nitrate production

E. Nitrophosphate production

A. AMMONIA PRODUCTION BY FUEL PARTIAL OXIDATION

1. INTRODUCTION

The production process of synthesis gas, developped up to now, use either waste heat boiler or water quench after synthesis gas generator.

A certain quantity of soot is produced, it can be extracted either in quench stage or after the stage of heat recovery.

Process which will be rapidly described is a partial oxidation using water quench mode (Texaco process).

2. DESCRIPTION

Raw material can be any fuel oil pumpable at temperatures below around 200°C, and with a sulfur content below or equal to 6 % wt.

Fuel oil is at first pumped at high pressure, about 95 bars, then mixed with an appropriate quantity of superheated steam and the mixture comes in the synthesis gas generator. Oxygen produced in an air separator unit (included in the ammonia plant) is sent directly under pressure through this unit then preheated by steam before going to the generator where its disappears totally by reacting with fuel oil. Then gas is cooled by water quench in order to saturate it and to take out all the particles of soot made in this reaction.

The water-soot stream is extracted continuously and purrified in a two stages system, using an extraction by naphta at first, then by fuel oil. The soot-free water is recycled to the syn-gas scrubber and the fuel oil, with the soot, is totally recycled to the generator.

The clean gas without the soot passes through 2 reactors in serie, the two working with a medium temperature conversion (330°C). The catalyst can operate with a high sulfur content in the gas and can reduce the CO content of the shifted gas at a value below or equal to 1.5 % vol.

Heat of shifted gas is used to preheat the boiler water, process condensates and demineralized water. After final cooling, gas is sent to the rectisol unit in order to extract CO_2 and H_2S.

In the rectisol unit, gas is washed up to an almost sulfur free content and up to a CO_2 content of about 20ppm. And gases are selectively washed up and delivered separately :

- a stream of rich gaz in H_2S (about 15 to 20%) and containing all COS of synthesis gas, stream which will be sent to sulfur unit included in ammonia plant.
- CO_2 is sent either to the atmosphere, mixed with a certain quantity of stripping nitrogen, the mixture having a sulfur content below 5-10 ppm, or to the Urea unit.

The Rectisol process operates at a temperature of about - 10 - 20°C for the washing of H_2S and at about - 30°C for the washing of CO_2. The washed synthesis gas passes through a molecular sieve in order to eliminate the traces of methanol and CO_2, then is washed out with nitrogen where all the last traces of impurities (CO_2, CO, CH_4) are totally eliminated.

Then synthesis gas is sent to the centrifugal compressor which compress it.

Synthesis occurs in modern installations around 500°C at pressures ranging from 150 to 300 bars, depending on the process and the capacity of the installation.
The synthesis reaction is written as follows

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The equilibrium concentration of the ammonia is raised by increasing the pressure or lowering the temperature.

The iron catalyst is activated by oxides such as potassium, calcium, magnesium oxides, and aluminium oxide.

Processes vary according to the selection of operating parameters such as pressure, temperature, space velocity, and also depending on the type of temperature regulation selected. Large units are designed with regulation by injection of colder synthesis gas (reaction quenching) at different points of the catalyst bed (ICI) or between separate catalyst beds (M.W. Kellogg, M. Topse). This is generally combined with heat exchange between reactants and effluents, generally by means of an exchanger located in the reactor. The F. Uhde process design calls for heat exchangers between consecutive catalyst beds.

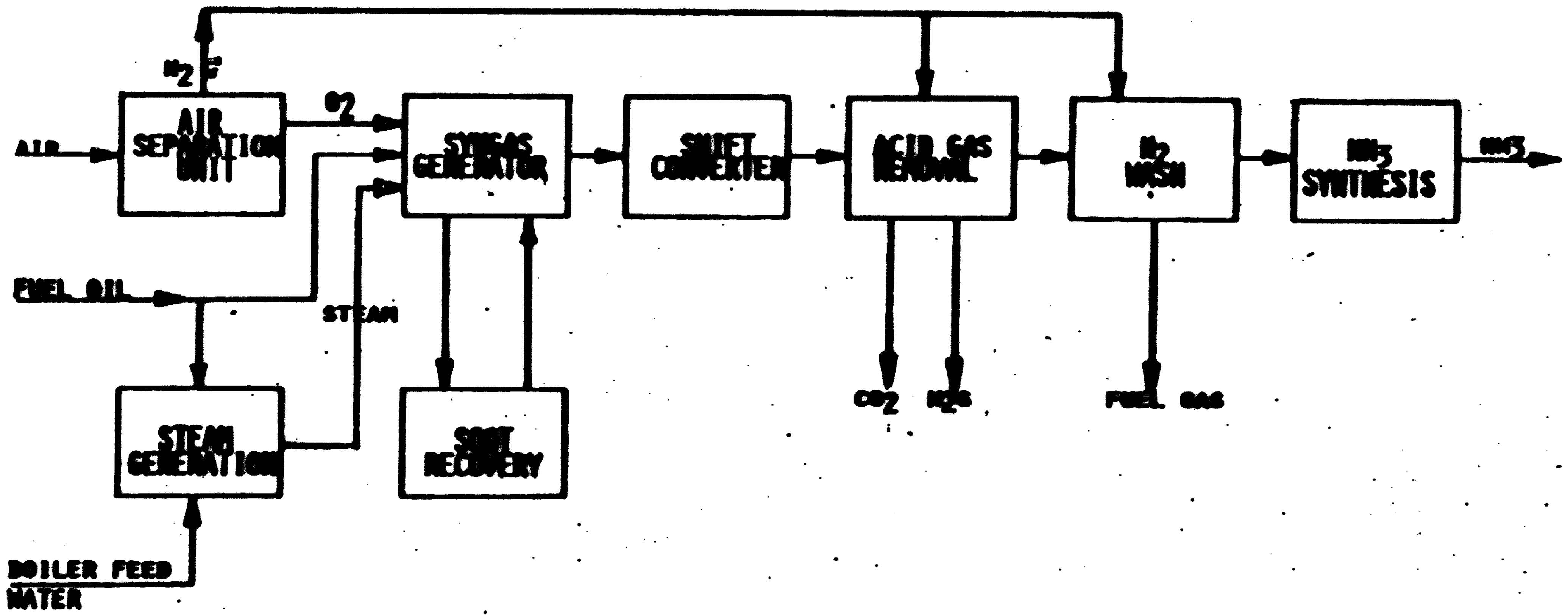
The heat available at high temperature is recovered by the effluent of the reactor, and used to preheat the feedwater or to produce steam.

Differences between the operating parameter levels in the different processes are reflected by different recycling rates. The ammonia content of the reactor effluent varies from 12 to 20 %, but the curve of production cost as a function of ammonia content is relatively flat and is not a good profitability criteria.

The recycled gas is mixed with the fresh charge at the exit of the main compressor, and the combined charge is compressed in the final stages of the compressor.

The reactor effluent is cooled by heat exchange in a feedwater preheater or waste-heat boiler, and by a series of heat exchangers followed by coolers. The ammonia is condensed and separates in a high pressure separator, from which the recycled gas is taken. The ammonia is cooled to -34°C by successive expansions to atmospheric pressure, and then sent to storage.

FLOW DIAGRAM FOR AMMONIA MANUFACTURE



B. UREA PRODUCTION

1. INTRODUCTION

Ammonia and carbon dioxide are the feedstocks in all present day commercial processes for the production of urea. They are reacted together at temperatures and pressures ranging from 170-210°C, 120-280 Kg/cm^2 respectively. The effluent from the synthesis reactor contains urea, water, excess ammoniac and subtantial quantities of ammonium carbamate, a reaction intermediate.
The principal reactions are :

$$CO_2 + 2NH_3 \rightarrow NH_2\,COO\,NH_4$$

$$NH_4\,CO_2\,NH_3 \rightarrow NH_2\,CO\text{-}NH_2 + H_2O$$

The first reaction is exothermic and goes rapidly to completion. The second is endothermic and is a relatively slow reaction.

Side reactions as biuret formation occur.

In all urea processes carbamate must be removed from the urea solution produced in the reactor. The difference in the various processes available are in the way the carbamate is decomposed and removed from the product and in the way in which the off-gases produced in the decomposition are treated.

Available commercial processes may be divided into four main groups.

- one through processes
- partial recycle processes
- total recycle processes
- stripping processes.

The description given hereafter, which is the description of the stamicarbon process, is only presented as an exemple and in no way presupposes the final choice of process.

2. DESCRIPTION OF THE PROCESS

The process by stripping, with total recycle and evaporation for the urea synthesis, includes the following stages :

- compression of NH_3 and CO_2
- synthesis
- recycling
- evaporation
- prilling

The reactor is a stainless steel vessel containing a series of trays to assist mixing of the reactants. As oxygen inhibits the corrosive action of the reaction medium traces of air are added to the carbon dioxide feed prior to compression.

Ammonium carbamate is stripped from the urea solution leaving the reactor by the fresh carbon dioxide feed. Stripping takes place at reaction pressure in a vertical steam heated tubular heat exchanger. Maximum steam pressure is 25 ats.g but pressures down to 18 ats.g are used.

Most of the unconverted carbamate dissociates into gaseous ammonia and carbon dioxide which pass to a condenser. There they recombine to form ammonium carbamate and most of the sensible heat of reaction is used to raise low pressure steam in the shell of the condenser.

In the reactor, optimum ammonia carbon dioxide mol-ratio is set up at 2.8 by adding to the gas coming from the condenser of which optimum ratio NH_3/CO_2 is 2.4, the required quantity of ammonia.

Reactor outlet temperature is in the range of 180-190°C and the pressure is approximatively 130 Kg/cm^2.

The reactor is sized to give a residence time of 45-60 minutes giving an approach to equilibrium of 90-95 per cent and ensuring stability of operation at varying feed rates.

On leaving the stripper, the urea solution is let down in pressure to 2-5 bars, clear out of residual ammonia and carbon dioxide and some water in a rectification column. These products are cooled and sent back to the high pressure condenser.

The solution coming from the rectification column is let down and sent to the flash drum.

During the let down of the solution, a big quantity of ammonia vapor and water leaves the solution causing thus a decrease of temperature.
The urea content of the solution is about 75%. The solution is sent to the storage tank of urea solution.

The solution urea pump transfers the solution to the heater of the first stage of evaporation. In this one pass exchanger, the urea concentration is increased to 95%. The vapor phase, separated from the liquid in a separator, is condensed in the condenser of the first stage of evaporation.

The vapors of the flash drum are condensed and sent back to the BP scrubber with some ammoniacal condensates coming from the other condensers.

The urea solution flows from the first stage of evaporation to the second stage.

The second stage of evaporation includes in theory the same equipments than the first stage.

The mixture liquid/vapour flows from the heater towards the separator. The vapour is drawn in the ejector-condenser group where it is condensed. The condensates are sent to the tank of ammoniacal water.

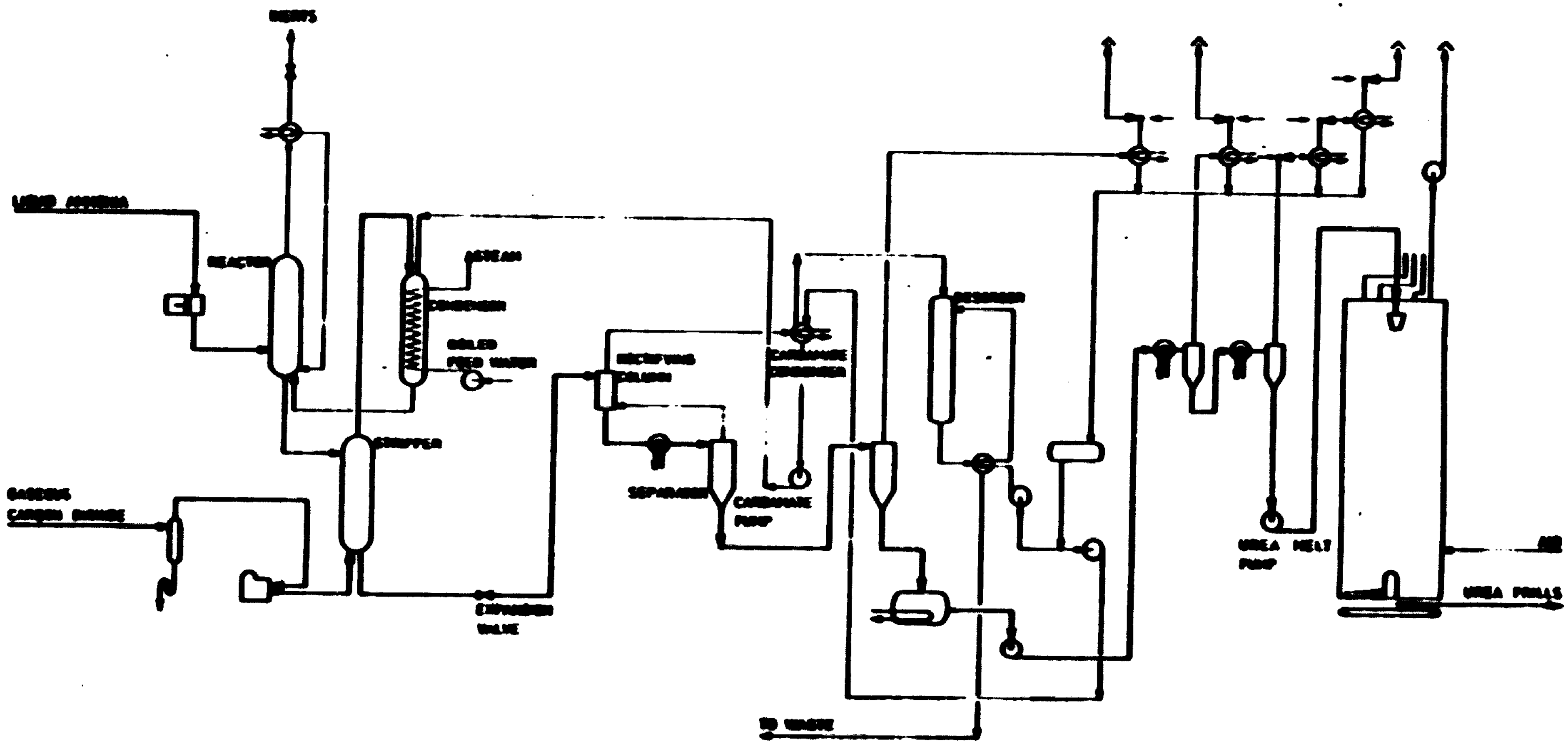
The noncondensable gas coming from the condensers are exhausted to the atmosphere.

The concentrated urea solution is sent to the suction of the melted urea pump.

The melted urea is sent to the top of the prilling tower.

The prilling basket delivers the melted urea in small droplets in all the section of the tower. During their fall in the tower, the droplets are solidified. The cristallisation heat is recovered by the air drawn in the column by ports located in the lower part.

The urea prills are recovered at the bottom of the tower where a scraper feeds a belt conveyor which carry then to the storage.



UREA PLANT
STRIPPING PROCESS

C. NITRIC ACID PRODUCTION

Nitric acid is produced by the oxidation of ammonia. This technique is practically the only one employed at present. The synthesis occurs in three consecutive stages corresponding to the following chemical reactions :

- phase 1 : oxidation of ammonia in a burner :

  $4NH_3 + 5O_2 \rightleftarrows 4NO + 6H_2O \quad \Delta H = 216.6$ Kcal
  (platinum catalyst)

- phase 2 : oxidation of nitrogen oxide in a cooling condenser :

  $2\ NO + O_2 \rightleftarrows 2NO \quad \Delta H = 27{,}1$ Kcal

- phase 3 : absorption of nitrous gases in an absorption column :

  $3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO \quad \Delta H = 32{,}2$ Kcal

Several alternatives are available based on this scheme, as a function of the pressures adopted in each phase. The first processes employed were monopressure processes in which the same pressure was employed in the different phases. More recently, dual pressure processes, in which the absorption pressure is higher than the oxidation pressure, have been introduced.

Although the complete pressure range between 1 and 9 bars can be employed, industrial processes employ the following pressure levels in practice :

. low pressure (LP)	1 bar absolute
. intermediate pressure (IP)	4 to 6 bars absolute
. high pressure (HP)	7 to 9 bars absolute

The following combinations are the most widely used in practice.

	oxidation	absorption
. case 1 (dual pressure)	LP	IP
. case 2 (monopressure)	IP	IP
. case 3 (dual pressure)	IP	HP
. case 4 (monopressure)	HP	HP

In case 3, the absorption pressure is generally raised to about 12 bars.

The choice is generally limited between a high pressure process and a dual pressure process (IP + HP).

But at this stage of the study, it is not possible to choose definitively between the two types.

The description given hereafter which is the description of dual pressure process (IP + HP) is only presented as an exemple and in no way presupposes the final choice of process.

A flowsheet of the process is given in Figure 3.

In principle, the dual pressure processes are closely similar. Differences are essentially of a technological nature, dealing mainly with the technology of the oxidation reactor, the heat exchange circuit, and the packing and design of the absorption tower.

Oxidation of ammonia to nitric oxide NO

The liquid ammonia is evaporated in a reboiler and then superheated to about 150°C. The ammonia vapors are then filtered. Moreover, the process air is compressed to about 5 bars after filtration. A filter located downstream from the compressor eliminates oil traces and other impurities liable to damage the catalyst. For the rest of the process, the equipment is constructed of stainless steel.

The gaseous ammonia and air streams are mixed and enter the oxidation reactor (s). The latter contains the platinum-rhodium catalyst (about 90-10) which promotes equilibrium kinetics. The catalyst consists of gauze of woven 4 to 6/100 mm wire weighing about 450 g/m^2. A distributor device permits proper distribution of the gas stream over the gauze. The temperature in the reactor is about 850°C. The heat of reaction is recovered by successive passage of the gases through a steam superheater, a boiler, and a feedwater heater.

A cooling condenser eliminates condensates which are recovered and sent to the absorption unit by means of the separator.

Nitrous vapors are sent to the compressor.

(NOTE : some conversion of nitric to nitrous oxide occurs in the cooling condenser).

Absorption unit

The absorption unit also comprises acid bleaching (denitration), oxidation of nitric oxide and absorption proper. The hot air current from the compressor is cooled and sent to the bottom of the bleaching column, eliminating dissolved nitrogen oxides, and giving a perfectly clear acid, which is sent to storage.

The air leaving the top of the bleaching column is mixed with the nitrous vapors upstream from the compressor.

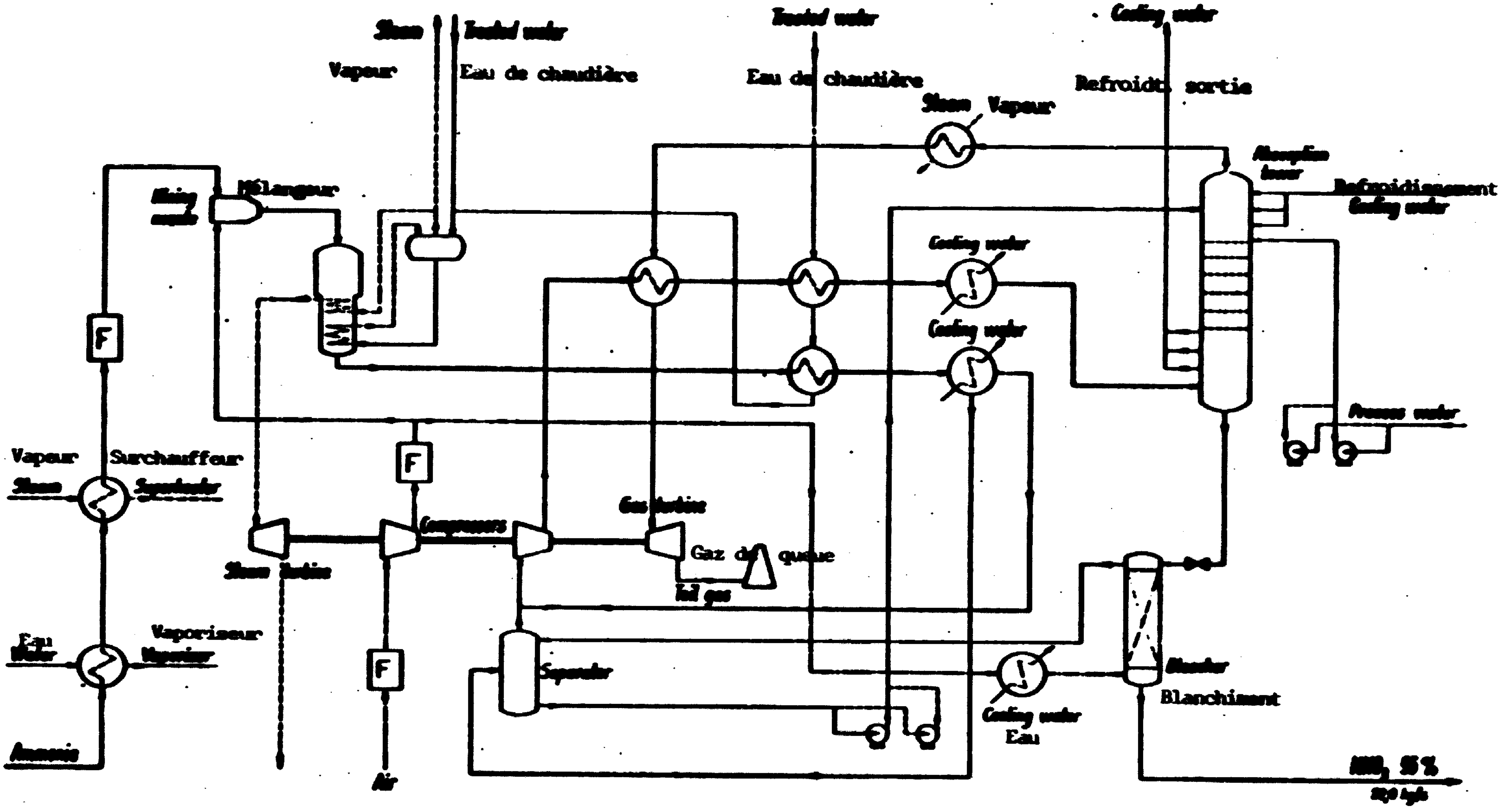
The compressor raises the gases to a pressure which is generally about 12 bars.

The gases leaving the compressor are cooled by heat exchange with the tail gases in a boiler feedwater heater, and finally in a water-cooled heat exchanger.

The low temperature level (about 30°C) reached and the pressure favor conversion of the monoxide into the dioxide, which occurs at the bottom of the absorption tower.

The gases are then introduced into the absorption tower, where they are absorbed by the condensates coming from the cooling condenser and by the process water. The excess air permits gas phase oxidation of the nitric oxide produced during absorption. A cooling circuit eliminates the heats of oxidation and absorption in the tower. The 55 to 60 % nitric acid produced is sent to the column before storage.

The gases leaving the top of the absorption tower contain less than 200 ppm of nitrogen oxides in a suitably designed column. (A lower nitrogen oxide content requires a more expensire absorption tower.) These gases are expanded in a gas turbine before being discharged through the stack.



NITRIC ACID PRODUCTION
(BI PRESSURE PROCESS)

D. 33.5 % AMMONIUM NITRATE

The production of ammonium nitrate by neutralization of nitric acid with ammonia, is the only industrial method currently employed for this purpose, with the exception of small-scale production from calcium nitrate, a by-product of certain processes involving nitric acid attack of phosphate ores.

The synthesis occurs in accordance with the following exothermic reaction :

$$NH_3 + HNO_3 \rightarrow \underset{\text{(in solution)}}{NH_4NO_3} \qquad H = 26 \text{ Kcal/mole}$$

The ammonium nitrate is produced either in solution or molten, depending on the process. It is then granulated, crystallized or prilled. The main processes differ according to the method employed for neutralization (under pressure, at atmospheric pressure or under vacuum), and by the technique employed to produce the dry nitrate).

Nevertheless, for the production of nitrogen fertilizers, "prilling" is almost universally used.

Modern ammonium nitrate production processes hence involve the following phases :

- neutralization,
- concentration,
- prilling,
- coating/adding additive.

Neutralization can be effected at atmospheric pressure or under about 4 bar pressure (vacuum neutralization is only used for the production of crystallized ammonium nitrate).

In modern processes, the ammonium nitrate solution is concentrated in two stages :

- to 95 % without external make up energy,
- to 99,7 % by final evaporation.

This two-stage concentration operation is designed to limit a minimum the residence time in high concentrations, as the second concentration is effected immediately before introduction into the prilling tower from a 95 % ammonium nitrate recovery tank. The choice of a high concentration is dictated by savings in investment and operating costs in the pearling tower.

In view of the hygroscopic nature of the nitrate, agglomeration of the prills should be prevented by spraying with an anti-caking agent.

Description of the process

In their basic principle, the major processes do not exhibit any fundamental differences. They only differ on technological points associated with the use of specific equipment, or in systems used for heat exchange between the different fluids.

Figure 4 shows a typical simplified flowsheet of an ammonium nitrate plant with reutralization carried out under 4 bars pressure.

After preheating (generally by basic steam from the neutralizer). the nitric acid and ammonia are introduced into the neutralizer, which operates at about 130°C under 4 bars pressure.

The basic steam (containing a little ammonia) leaving the top of the neutralizer goes through a separator, which recycles the droplets of nitrate carried off from the neutralizer. This steam is used mainly to heat the primary evaporator. The surplus can be used for other purposes outside the nitrate plant, or condensed in the installation. The basic steam condensates are employed as process water in the nitric acid unit.

The ammonium nitrate solution leaving the bottom of the neutralizer contains about 78 % product. It is concentrated to 95 % in a falling film type evaporator operating under vacuum and heated by the basic steam.

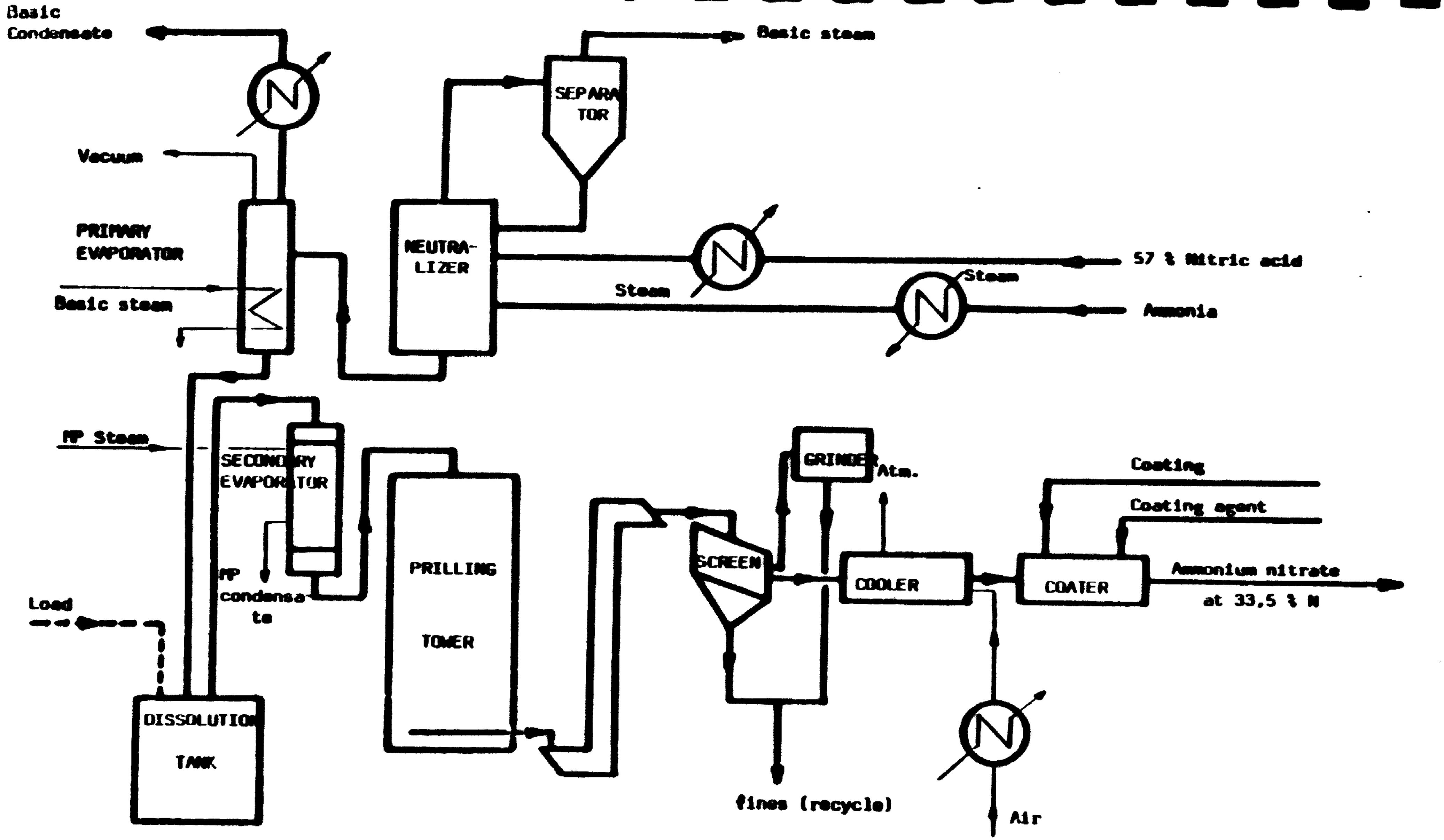
The solution is then sent to an intermediate tank, from where it is drawn off to a secondary falling film evaporator. The latter is heated by intermediate pressure steam (about 15 bar). The use of falling film evaporators eliminates the risk of decomposition of the ammonium nitrate.

The 99,7 % nitrate solution is then sprayed at the top of a prilling tower. It is then transformed into prills via nozzles or rotary basket.

The beads fall freely against a counter-current of air sucked up by fans located at the top of the prilling tower. Part of the air employed is obtained from the downstream coolers.

The ammonium nitrate leaving the prilling tower is screened in order to eliminate fines and lumps which are recycled.

The ammonium nitrate beads are then cooled with air in a cooler which is generally of the fluidized bed type. The air may be preheated with steam if necessary. The ammonium nitrate is then sent to a drum coating machine in which it is sprayed with an anti-caking product. It is then sent to the bagging installation by conveyor belt.



AMMONIUM NITRATE PRODUCTION
(PROCESS FLOW SCHEME)

E. NITROPHOSPHATE PRODUCTION

1. INTRODUCTION

During the past ten years several processes have been developped in order to produce nitrophosphate fertilizers with high water solubility of the phosphorus component. All of these processes seek to separate the phosphoric acid and calcium nitrate which are the two principal components in the phosphate rocknitric acid attack solution.

Three major types of process are the following :

- calcium nitrate crystallization processes
- phospheric acid extraction processes
- calcium sulphate precipitation processes

The description given hereafter, which is the description of the Norsk hydro process, is only presented as an exemple and, in no way, presupposes the final choice of process.

2. PROCESS DESCRIPTION

This process is divided in 4 sections :

- section 1 : phosphate dissolution
- section 2 : crystallization and neutralization of calcium nitrate
- section 3 : neutralization of the mother liquor, evaporation, mixing and granulation
- section 4 : conversion of calcium nitrate.

Phosphate dissolution

Reactions :

a) $3Ca_3(PO_4)_2 CaF_2 + (20 + x)HNO_3 \rightarrow 6H_3PO_4 + 10Ca(NO_3)_2$
$+ 2HF + xHNO_3$

b) $Ca CO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + CO_2 + \overset{H}{H_2O}$

Fluor leaves the reactor as SIF_4 and HF associated with nitrogen oxides and little CO_2. This mixture is washed in scrubbers. Phosphate is dissolved in excess 58 - 62 % nitric acid. The excess prevents the precipitation of calcium phosphate during the crystallization. If the quantity of acid is reduced, a fertilizer with a minimum ratio N/P_2O_5 of 0.6/1 can be produced directly.

If the phosphate rock is poor, a sand trap is installed after the dissolution.

Crystallization and filtration of calcium nitrate $Ca(NO_3)_2\ 4H_2O$

The phosphate solution coming from the reactor is a mixture of nitric and phosphoric acids, with calcium nitrate. This solution feeds crystallizers which are agitated tanks cooled by chilling coils.

The crystallization is carried out in a number of tanks in series in order to ensure a continuous production.

The final temperature depends upon the required content of the water soluble $P_2O_5$and the "nutrient" concentration.

Neutralization, evaporation

The mother liquor coming from the filtration of calcium nitrate is neutralized by gaseous ammonia as indicated in the following reactions.

a) $H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$

b) $H_3PO_4 + 2NH_3 \rightarrow (NH_4)_2\ H\ \ PO_4$

c) $HNO_3 + NH_3 \rightarrow NH_4NO_3$

d) $Ca(NO_3)_2 + 2HF + 2NH_3 \rightarrow 2NH_4NO_3 + CaF_2$

e) $Ca(NO_3)_2 + CaHPO_4 + 2NH_3 \rightarrow 2NH_4NO_3 +$

The impurities are precipitated as complex salts. The neutralization is carried out in two stages in order to decrease the viscosity which increases because of the intermediate values of PH (each phosphate must be tested in laboratory). Moreover, the neutralization of the ratio nitrogen / P_2O_5 is adjusted by addition of the ammonium nitrate. The water content of the neutralized liquor is reduced to about 0.5 % by evaporation. Then residu is mixed either with potassium chloride or with potassium sulfate before prilling. The NP melt or NPK mixture is formed into "drops" in the top of the prill tower by means of a rotating perforated prill bucket. The solidified prills are removed from the tower with a rotating tower bottom or a rotating scraper. The off-size prills are grinded and recycled. Then the prills are coated before being storaged.

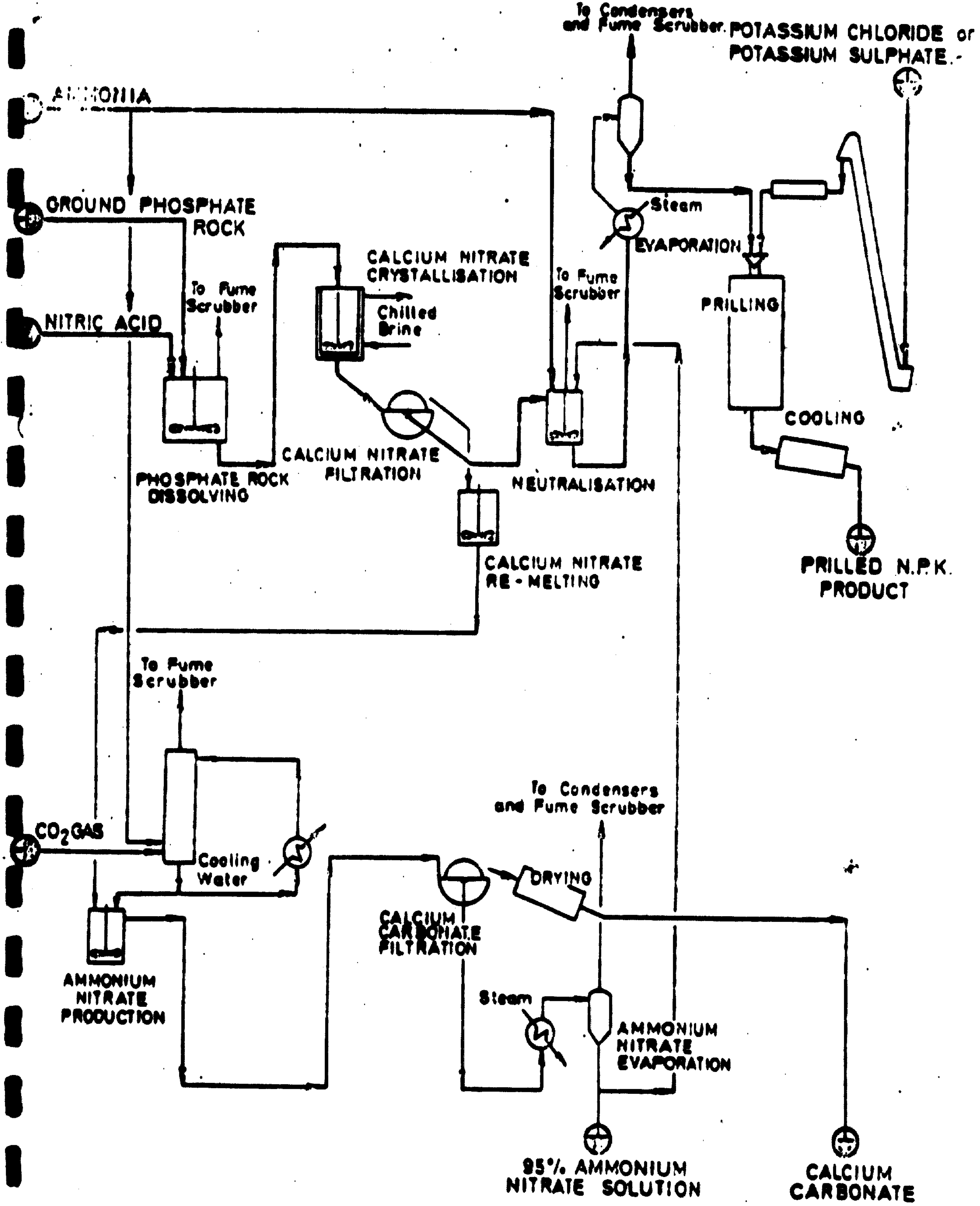
Calcium nitrate conversion

Calcium nitrate coming from the filtration stage is reintroduced in the tanks of agitation where it is mixed with ammonium carbonate obtained by reacting ammonia with carbon dioxide in the solution of ammonium nitrate.

Calcium carbonate produced is filtrated and the mother liquor which is nitrate solution is withdrawed.

The cake is transformed again in slurry which is filtrated again and washed strongly in order to obtain calcium carbonate which can be used.

The advantages of this conversion are due to the quality of calcium carbonate. Moreover ammonium nitrate is very pure and the crystals of calcium carbonate are easily filtrated and washed.



SIMPLIFIED FLOWSHEET

ANNEXE 2

STEAM REFORMING OF GAS

The basic scheme of synthesis gas production in steam reforming of naphta and of gas is the same, except small difference.

In order to switch from natural gas to naphta, equipment of naphta vaporization and naphta desulfurization must be added. Moreover the catalyst of primary reformer must be replaced by special catalysts for naphta and decarbonation capacity must be increased.

To switch from naphta to natural gas, it is necessary to increase appreciably the heating capacity of primary reformer. Cracking natural gas requires more heat and the skin temperatures of tubes must be higher but it is the only big change required in this case.

Investments of ammonia plant based on natural gas are 7 - 8 % lower than those of ammonia plant based on naphta.

Average consumptions for natural gas steam reforming are given in the table 1.

In the following tables, an economic comparison between steam reforming of naphta, steam reforming of gas and fuel partial oxidation is presented.

TABLE 1

AVERAGE CONSUMPTION PER TON OF AMMONIA

Natural gas (process + fuel)	in 10^6 Kcal	8.80
Cooling water	in m^3	270
Process water	in m^3	5

TABLE 2

INVESTMENTS

in 10^3 US $

	Steam reforming of naphta	Steam reforming of gas	Fuel partial oxidation
Process units	69 000	64 600	92 000
Off-sites	34 500	32 300	46 000
Erected cost in Europe	103 500	96 900	138 000
Total cost in Europe	119 025	111 435	158 700
Total cost in Vietnam	177 359	166 038	236 460
Spare parts	6 180	5 785	8 240
Catalysts and chemicals	900	380	450
Royalties	2 500	2 500	2 500
Pre operating expenses and start up expenses	12 420	11 620	16 550
Total investment excluding financial charges	199 350	186 300	264 200
Working capital	6 700	6 700	6 700

TABLE 3

RAW MATERIALS AND UTILITIES CONSUMPTION

	Steam reforming of naphta		Steam reforming of natural gas		Fuel partial oxidation	
	Per ton of NH_3	Per year	Per ton	Per year	Per ton of NH_3	Per year
Naphta process in tons	0.524	172 920				
Fuel in tons	0.392	129 500				
Natural gas in 10^6Kcal			8.90	2 937 000		
Industrial water in m^3	22	7 280 000	15.5	5 105 000	23.5	7 755 000
Fuel oil (process + fuel) in tons					0.935	308 550

TABLE 4

OPERATING COSTS IN 10^3 US$

	Steam reforming of naphta	Steam reforming of gas	Fuel partial oxidation
Variable charges			
. Fuel	-	-	26 844
. Natural gas *	-	25 551	-
. Naphta	26 975	-	-
. Fuel LSC	11 655	-	-
. Industrial water	363	305	388
. Catalysts and chemicals	1 200	480	420
Sub-total	40 193	26 336	27 652
Fixed charges			
. Manpower	195	195	195
. Technical assistance	39	39	39
. Maintenance	3 090	2 890	4 120
. Insurance	1 195	1 120	1 585
. General overhead	70	70	70
. Land rent	30	30	30
. Interest on working capital	670	670	670
Sub-total	5 290	5 014	6 709
TOTAL OPERATING COST	45 383	31 350	34 361

Gas price is based on the price of calorie, i.e. 8.7 US $/$10^6$ Kcal.

Results

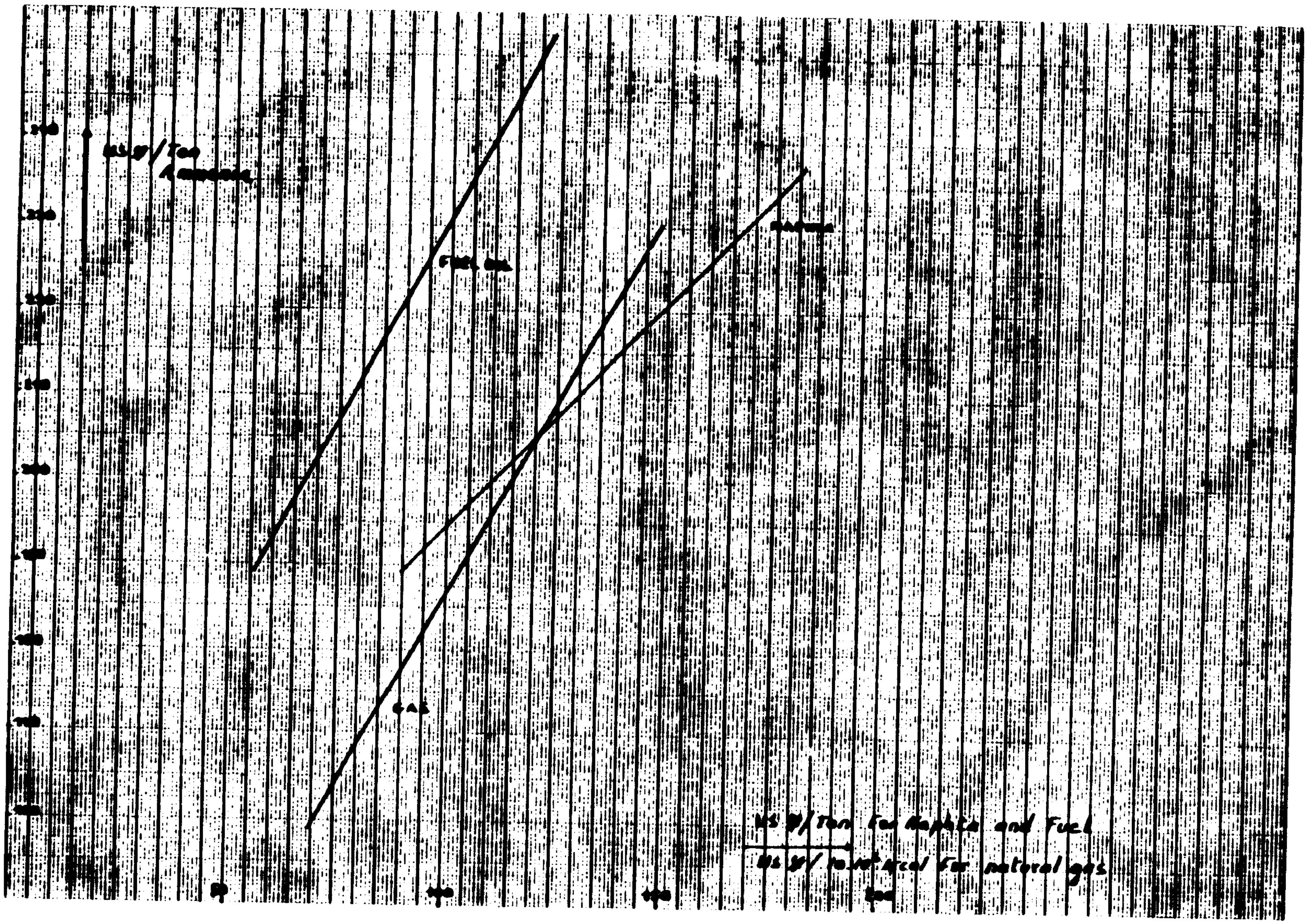
Assuming before taxes payment times of 7 years, for each type of processes, ammonia prices has been calculated for several raw materials prices. Results are given in table 5.

The following figure gives the variation of ammonia prices versus feedstocks prices for different routes of production and for the same profitability (pay out time = 7).

TABLE 5

ECONOMIC COMPARISON OF DIFFERENT ROUTES OF AMMONIA PRODUCTION

	Naphta steam reforming			Steam reforming of gas			Fuel partial oxidation		
Investment in 10^3 US $	198 350			186 300			284 200		
Pay out time	7			7			7		
Gross cash flow in 10^3 US $	37 740			28 470			26 814		
Raw material Price : US $	156 per ton	140 per ton	175 per ton	8.7 per 10^6Kcal	7.0 per 10^6Kcal	10 per 10^6Kcal	87 per ton	70 per ton	100 per ton
Ammonia price US $/ton	224	215	234	175	160	187	218	202	230


US $/Ton Ammonia
FUEL OIL
GAS
US $/Ton for Naphtha and Fuel
US $/10⁶ Kcal for natural gas

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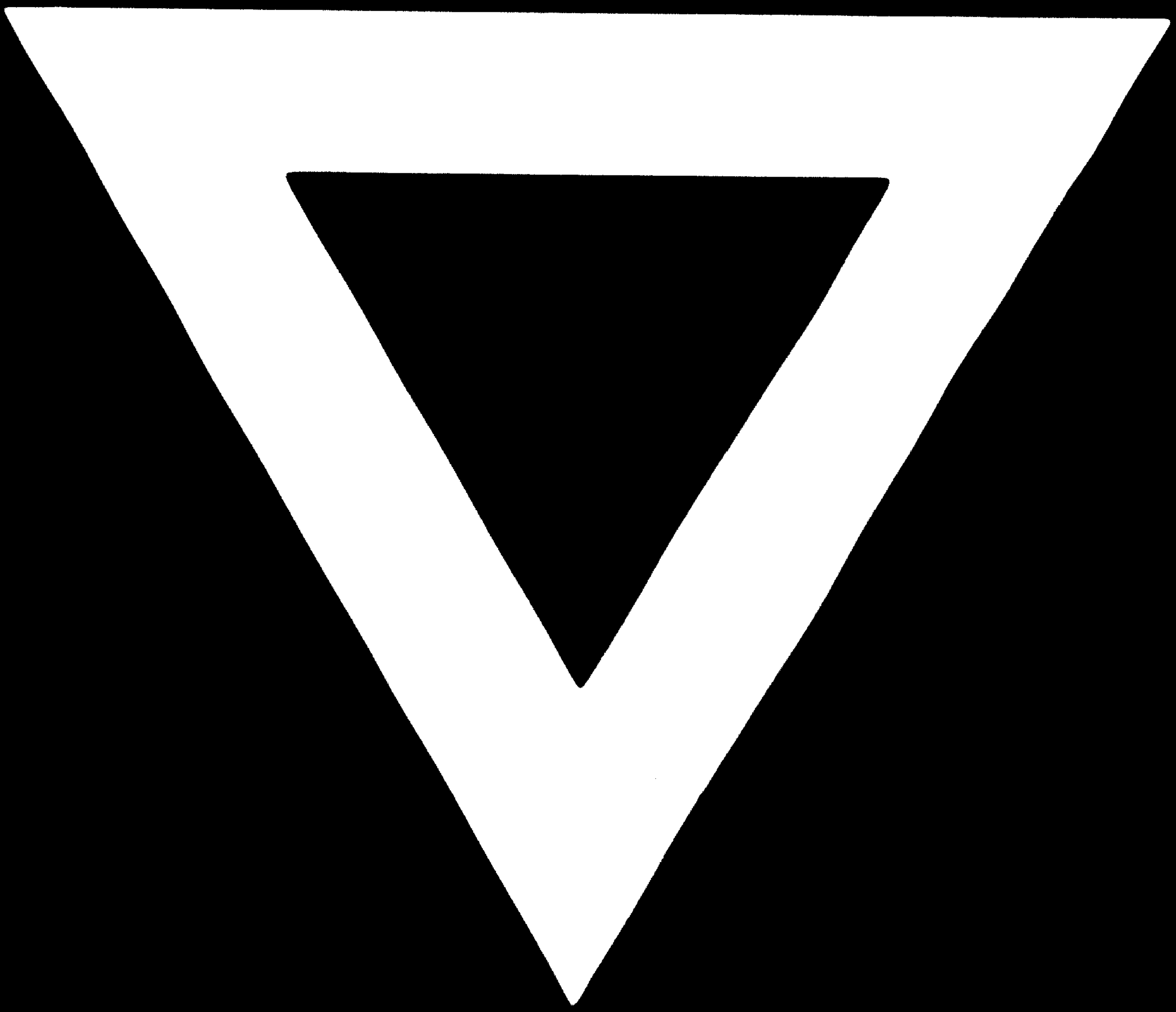

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