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Complex Fertilizers Based on the Nitric Acid Decomposition of Phosphates

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The conditions governing the equilibrium in the reaction of fluoroapatite and mineral admixtures in natural phosphate raw materials with nitric acid and also certain problems of the kinetics of the decomposition of phosphate minerals are considered in the review. The principles of several technological schemes in the manufacture of Nitrophoska are described. The most important trends in new studies designed to obtain complex fertilizers by the decomposition of phosphates with nitric acid are also indicated. It is concluded that a promising method for the manufacture of Nitrophoska involves a procedure with cooling, retaining the main, fruitful idea of employing for the decomposition of phosphates nitric acid without the addition of other acids or their salts.
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I. INTRODUCTION

The method of processing natural phosphates with nitric acid proposed in 1908 by Pryanishnikov and Britske[1,2] for the manufacture of a phosphate fertilizer [$CaHPO_4$ (precipitate) and a nitrate fertilizer (calcium nitrate)] could not find wide application before the end of the First World War, since at that time there was no synthesis of ammonia and its oxidation to nitric acid on an industrial scale.

In recent years, with the rapid and powerful growth of the manufacture of synthetic ammonia developing along progressive and economical lines, there has been a greater possibility of obtaining cheap nitric acid and its employment not only for the above two single fertilizers but also, and mainly for combined (complex) fertilizers — nitrophosphates (Nitrophos and Nitrophoska) containing nitrogen, phosphorus, potassium, and other nutrient elements.

The growing importance of the manufacture of fertilizers based on the nitric acid decomposition of phosphates together with their processing by sulphuric acid, which has been developing most rapidly, arises because nitric acid is employed in two ways in the decomposition of phosphates: as a source of active hydrogen ions and as a carrier of nitrogen — a useful component of fertilizers.

In the most rational process unpleasant waste is not formed, as happens in the sulphuric acid decomposition of phosphates, accompanied by the formation of phosphogypsum, which has so far not found a useful application.

The employment of nitric acid permits a more complete extraction of fluorine and lanthanides from apatite An advantage of nitric acid is also the possibility of using as a starting material low-grade phosphorites containing considerable amounts of iron and aluminium compounds.

The method of nitric acid processing of phosphate raw materials has undergone extensive development since the initial studies carried out at the Fertilizers, Insecticides, and Fungicides Research Institute (NIUIF) from 1925[3–5]. Some of the versions of the manufacture of simple and complex fertilizers from nitric acid – phosphoric acid solutions investigated in the Soviet Union and elsewhere have not found large-scale applications, while others have been improved and have assumed a dominant position under modern conditions.

Technological nitric acid processing of phosphates includes the following main stages: (1) intrinsic decomposition of the phosphate raw material with nitric acid; (2) isolation of calcium from the nitric acid – phosphoric acid solution obtained after the decomposition of the phosphate; (3) neutralisation of the solution with ammonia (ammoniation) or lime; (4) conversion of the neutralised solution into a fertilizer †. In certain versions the processing of phosphates includes additional operations such as the separation from solution of the insoluble residue, the decomposition of sodium or potassium fluorosilicate, and precipitation of lanthanide phosphates.

The above stages in the manufacture of nitrophosphates are involved in a close interrelation, the nature of which is described below for individual specific procedures.

II. PHOSPHATE DECOMPOSITION PROCESSES

In a general form the decomposition of fluoroapatite with nitric acid can be represented by the equation:

$$Ca_5(PO_4)_3F + 10\,HNO_3 = 3H_3PO_4 + 5Ca(NO_3)_2 + HF + 290\ \text{kJ mole}^{-1}. \quad (1)$$

Under the industrial conditions of the interaction with nitric acid at a concentration of 50–55%, the reaction temperature is maintained at 50–60°C mainly as a result of the heat of reaction (1)[6,7].

The conditions governing the equilibrium in this process have been established with some approximation by means of a graphical analysis of the $CaO–P_2O_5–N_2O_5–H_2O$ system, which was investigated at 0°, 5°, 25°, 50°, 75°, and 100°C. The metastable state of the system at 50°C was also investigated[11].

In the acid regions of the diagram of the system the following solid phases in equilibrium with saturated solutions at the above temperatures were discovered: $Ca(NO_3)_2$ (tetrahydrate, trihydrate, dihydrate, and the anhydrous

† The present review is restricted to the analysis of the manufacture of solid fertilizers only and does not deal with the specific problems of the synthesis of liquid and suspension fertilizers based on the decomposition of phosphates with nitric acid.

salt), $Ca(H_2PO_4)_2.H_2O$, and $CaHPO_4$. More basic phosphates, including hydroxy-apatite, are found only in a narrow region of highly dilute solutions.

The main conclusion from the analysis of the system is that in the interaction of fluoroapatite with a stoichiometric amount [according to Eqn. (1)] of nitric acid (at a concentration of 47% and above) the phosphate should be completely decomposed following the attainment of equilibrium. Indeed, experimental conditions have been found ensuring in practice a high (98–99%) degree of decomposition of natural phosphates at 45–60°C [12-17].

The study of the 50° isotherm (in the equilibrium and metastable states) by the method of "secondary projections" of the system showed[18,19] that, within the limits of the nitric acid concentrations employed under technological conditions (47–60%) in amounts relative to stoichiometry corresponding to 100–140%, the composition point *C* of the resulting solutions is in the crystallisation region of $Ca(H_2PO_4)_2.H_2O$ (Table and Fig. 1). These data show that the decomposition of fluoroapatite by nitric acid at 50°C proceeds in accordance with the following equation:

$$Ca_5(PO_4)_3F + 10HNO_3 = (3-n)H_3PO_4 + 0.5n\,Ca(H_2PO_4)_2 + (5-0.5n)Ca(NO_3)_2 + n\,HNO_3 + HF\,. \quad (2)$$

Thus both theory and industrial practice permit variation of the conditions governing the decomposition of phosphates within wide limits. This applies not only to the concentration and the specified amount of nitric acid but also to the process temperature. This situation favours the optimisation of the technological conditions in subsequent stages of the nitric acid process.

Conditions for the formation of $Ca(H_2PO_4)_2.H_2O$ in the nitric acid–phosphoric acid solution at 50°C.

Conditions	Stable equilibrium	Metastable equilibrium
Concn. of HNO_3, %	71.0—38.5	77.5—37.5
Amount of HNO_3 relative to stoichiometry, %	116.5—93.6	158.0—109.0

Under the conditions of the decomposition of fluoroapatite at 50°C presented in Table 1, $Ca(H_2PO_4)_2$ and calcium nitrate are present in solution. Analysis of the equilibrium in the $CaO-P_2O_5-N_2O_5-H_2O$ system showed that calcium nitrate may be isolated from solution in the form of the anhydrous salt directly in the course of the decomposition of the phosphate at the same temperature, provided that nitric acid at a concentration in excess of 71% is employed in an amount exceeding 116.5% relative to stoichiometry. Therefore an experimental study was made of the decomposition of the apatite concentrate under the given conditions[18].

The study of the $CaO-P_2O_5-N_2O_5-CaSiF_6-H_2O$ five-component system at 60°C [20] showed that in the presence of potassium fluorosilicate and fluoride, formed on acid treatment of phosphates, the crystallisation regions of $CaHPO_4$ and calcium nitrate expand, while that of $Ca(H_2PO_4)$ contracts. Under certain conditions (low HNO_3 and H_3PO_4 concentrations in solution), this leads to the decomposition of $Ca(H_2PO_4)_2$ with deposition of $CaHPO_4$ in the solid phase:

$$Ca(H_2PO_4)_2 \rightleftarrows CaHPO_4 + H_3PO_4\,.$$

Calcium fluorosilicate can in turn decompose with formation of CaF_2 and SiO_2. The observed secondary phenomena can inhibit the decomposition of the phosphate raw material as a result of the formation of a crystalline crust on the phosphate grains and can also impede the separation of an insoluble precipitate. The complex processes associated with the presence of fluorine compounds in the system require further investigation.

The study quoted above[20] also revealed the favourable effect of free H_2SiF_6 in the phosphoric acid solution, which can partly or completely prevent the decomposition of $CaSiF_6$. In this connection it was of interest to determine the fluorine balance in the course of the nitric acid decomposition of natural phosphates.

In the processing of the apatite concentrate (process temperature 50°C) it was found that, when 55% nitric acid is employed, the bulk of fluorine (77%) passes to the liquid phase[21]. In the presence of 80% nitric acid, the evolution of fluorine into the gas phase (SiF_4) increases sharply—only about 18% of fluorine remains in the liquid phase[19]. The use of Karatau phosphorites also entails an increase in the evolution of fluorine into the gas phase—the degree of extraction of fluorine into the liquid phase in the presence of 55% nitric acid is about 58%.[21] The amount of fluorine in the insoluble residue is only about 1–3% of its content in the starting material.

The appreciable content of fluorine (H_2SiF_6) in the liquid phase necessitates its isolation: conditions have been developed[6,7,14,22] for the precipitation of Na_2SiF_6 from nitric acid – phosphoric acid solutions with the aid of a sodium nitrate (or sodium carbonate) solution. The gaseous fluorine compounds evolved are absorbed. The characteristic features of the absorption of HF and SiF_4 were investigated[23,24].

The direct requirement for sodium (or potassium) fluorosilicates is limited compared with the possible volume of their manufacture in fertilizer factories where phosphate raw materials are processed. For this reason, intense studies are being made at present on various versions of the manufacture from fluorosilicate – containing waste of products such as cryolite, aluminium, sodium, and ammonium fluorides, hydrofluoric acid, and others, the requirement for which increases from year to year[25-28].

The apatite concentrate contains about 0.9% of cerium-group lanthanides the bulk of which (98–99%) passes to the nitric acid – phosphoric acid solution. A process has been developed for the isolation from solution of lanthanide phosphates at 60–80°C and for 50% neutralisation of the first hydrogen ion dissociated from H_3PO_4 by lime, ammonia, or sodium carbonate to give a pH of 2–2.5.[29] The degree of precipitation of the lanthanides reaches 75–80%. The precipitate is separated from the solution by decantation. It is useful to treat the solutions by successive procedures – initially for the isolation of sodium fluorosilicate and then for the isolation of lanthanide phosphates. A number of other methods for their isolation have also been developed.

The kinetics of the decomposition of phosphate materials have not as yet been completely elucidated. Mainly experimental studies[6,7,14,16] were undertaken to investigate the influence of individual factors on the rate of reaction with nitric acid of the apatite concentrate and phosphorite from Krolevets, Izyum, Polpinsk, Zozh, Egor'evsk, Vyatsk, and Karatau deposits. These studies established

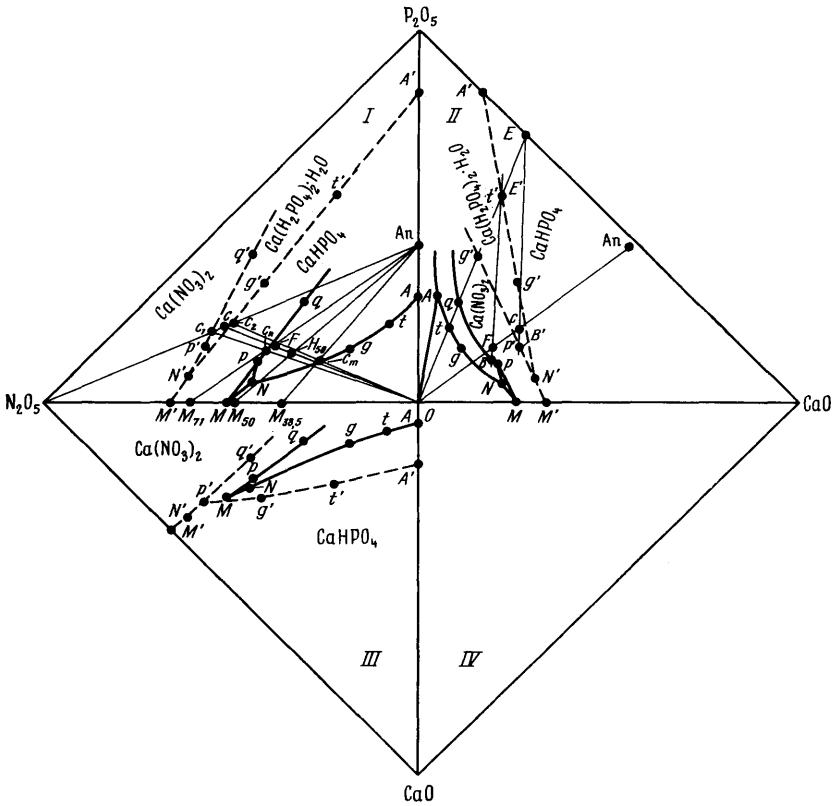


Figure 1. Graphical analysis of the $CaO-P_2O_5-N_2O_5-H_2O$ system at 50°C (decomposition of fluoroapatite with nitric acid)[18].

the principal relations: for example, the decomposition of phosphorites proceeds at a relatively high rate and the degree of extraction of P_2O_5 into the solution can reach 98–99% in the first 15–30 min. Apatite is decomposed by nitric acid more slowly — the reaction virtually reaches completion in the course of 60–90 min. The reason is that apatite is less reactive: its overall (external and internal) specific surface is smaller by a factor of 5–30 than that of phosphorites for the same degree of comminution[30].

The decomposition of natural phosphates accelerates with increase of temperature in the range 30–60°C. The temperature coefficient for each 10 deg C is about 1.3. With increase of the relative amount of nitric acid per unit amount of phosphate, the degree of neutralisation of the mixture of nitric and phosphoric acid falls, and therefore the rate of reaction increases.

The influence of the initial nitric acid concentration in the range 47–55% is small. It has been found[19] that, with increase of the HNO_3 concentration to 80%, a high degree of extraction of P_2O_5 into the solution is reached in about 3.5 h, mainly due to the precipitation under these conditions of $Ca(NO_3)_2$ crystals, which passivate the surface of phosphate grains.

The kinetics of the acid decomposition of phosphates have been investigated,[31–33] and it has been established that the interaction of apatite with inorganic acids under certain conditions (temperature and concentration) takes place entirely under diffusion-dependent conditions. The rate of reaction for 50% nitric acid is determined by the diffusion of ions from a temperature as low as 30°C. A study of the rate of decomposition of apatite by phosphoric acid[31] led to the conclusion that the driving force of the dissolution of apatite is the concentration gradient of calcium ions at the surface and in the bulk of the solution. In a study[32,33] of the kinetics of the interaction of apatite with acid, it was found that the rate of the process depends on the rate of diffusion of hydrogen ions to the interface, on the activity of hydrogen ions, on the solubility of the reaction products, and on the passivation of the surface by crystalline deposits (in this instance, of calcium nitrate), and also on the viscosity of the liquid phase and other physicochemical factors. The diffusion of H^+ and Ca^{2+} ions is accompanied by ion exchange (with NO_3^- and $H_2PO_4^-$ ions in the nitric acid decomposition), which accelerates the diffusion of the ion pair.

It has also been established experimentally[32,33] that under identical conditions the highest rate of reaction is obtained in the decomposition of apatites by hydrochloric and nitric acids: it is higher by a power of ten than in the reaction with phosphoric acid.

The behaviour of iron-containing impurities in the initial material is very important for the assessment of the nitric acid methods for the processing of phosphates. In a study of the kinetics of the decomposition by acids of the silicate mineral glauconite, which is present in phosphorites, it was established[31] that, despite the high degree of dissociation of nitric acid, it decomposes glauconite comparatively slowly. This is due to the formation of a dense SiO_2 envelope around the mineral grains, which inhibits

diffusion (passivation occurs). However, in the joint decomposition of such minerals together with phosphate, the resulting phosphoric acid accelerates the process. In practice, under continuous process conditions, the degree of extraction of $Fe_2O_3 + Al_2O_3$ into the solution amounts to about 70%. Iron and aluminium oxides react with phosphoric acid and form sparingly soluble phosphates, which leads to a loss of P_2O_5.

The presence of lower oxides of iron and also of organic substances in phosphorites leads to increased losses of nitric acid. On decomposition with nitric acid, low-grade phosphorites form considerable amounts of finely dispersed precipitates (mainly SiO_2), the separation of which by decantation or filtration is difficult.

One of the methods[6,7,12] for the decrease of the harmful influence of impurities in phosphorites in the course of nitric acid processing, which has been investigated, is heat treatment of the phosphorites. Optimal oxidative roasting conditions, which diminish the dissolution of iron and aluminium oxides, eliminate the losses of nitric acid, and improves the properties of the precipitates facilitating their decomposition, have been established for various phosphorites (from the Egor'evsk, Vyatsk, Polpinsk, Sozh, and other deposits). Thus heat treatment of phosphorites converts them into a starting material suitable for conversion by nitric acid into complex fertilizers without secondary enrichment.

The study of the problem of the separation of the insoluble residue formed in a finely dispersed state in the decomposition of the Karatau phosphorite is very important. The formation of the precipitate has been investigated[34,35] and methods and apparatus for the accelerated filtration of the sludge have been recommended.

III. ISOLATION OF CALCIUM FROM NITRIC ACID-PHOSPHORIC ACID SOLUTIONS AND ITS NEUTRALISATION

In the conversion of nitric acid–phosphoric acid solutions into fertilizers free phosphoric and nitric acids are neutralised. Technological processes based on the neutralisation of the solutions with lime or limestone, with precipitation and isolation of $CaHPO_4$ and formation of calcium nitrate as a second product were developed initially[14,36-40]:

$$3H_3PO_4 + 5Ca(NO_3)_2 + 3CaCO_3 \rightarrow 3CaHPO_4 + 5Ca(NO_3)_2 + 3CO_2 + 3H_2O. \quad (3)$$

A version of the synthesis of ammonium nitrate from calcium nitrate by treatment with ammonium carbonate solution was investigated:

$$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightarrow 2NH_4NO_3 + CaCO_3. \quad (4)$$

This method for the preparation of the citrate-soluble $CaHPO_4$ and of the low-percentage (15% N) hygroscopic calcium nitrate has been applied on a limited scale[41,42].

The possibility of obtaining from nitric acid–phosphoric acid solutions of the water-soluble $CaHPO_4$ (instead of the citrate buffer-soluble $CaHPO_4$), discovered in a graphical analysis of the $CaO-P_2O_5-N_2O_5-H_2O$ equilibrium system[3], should be noted. This version merits technical development.

The common procedures for the preparation of complex nitrogen-phosphorus fertilizers include the neutralisation of phosphoric and nitric acids with ammonia. Ammonia, which is the primary product of the fixation of atmospheric nitrogen, is now the most readily available, the most concentrated, and the cheapest nitrogen carrier, which accounts for the attempts to introduce nitrogen into complex fertilizers in the form of ammonia to the maximum possible extent

The phosphoric acid obtained by the sulphuric acid decomposition of phosphate is neutralised with ammonia, which results in the formation of fertilizers (Ammophos or Diammophos), which contain between 5.2 and 2.6 P_2O_5 units per unit weight of nitrogen. Depending on the initial phosphate material, Ammophos contains different amounts of P_2O_5 in a water-soluble form: for example 95% in the processing of the apatite concentrate and 75–80% in the processing of the Karatau phosphorite.

Numerous agrochemical studies led to the discovery that the majority of soils can assimilate almost equally readily both water-soluble and citrate-soluble forms of phosphate fertilizers. In the USSR the Government Standard GOST 11 365-65 specifies that in Nitrophoska not less than 55% of the P_2O_5 assimilated must be in a water-soluble form.

Mention should be made of the current trend in world practice to increase as far as possible the content of water-soluble P_2O_5 in fertilizers, which may be accounted for by the greater universality of the use of water-soluble P_2O_5 under various natural conditions.

In accordance with the requirements of agriculture, agrochemical science has established for various types of soil and agricultural crops specific and most widely used weight ratios of nutrient elements ($N-P_2O_5-K_2O$) in complex fertilizers. Fertilizers meeting these requirements have been conventionally termed balanced. A considerable proportion of the balanced fertilizers should have the ratios $N : P_2O_5 : K_2O = 1 : 1 : 1$.

Owing to its relatively low nitrogen content, in most cases Ammophos is not a balanced product. Therefore, it is either mixed with nitrogen fertilizers (ammonium nitrate, carbamide) or a mixture of ammonium phosphate and nitrate (Nitroammophoska) the composition of which is defined by the formula 17 : 17 : 17 (95% of P_2O_5 is in a water-soluble form), is produced.

Nitroammophoska is a complex fertilizer obtained by the sulphuric acid processing of natural phosphates. It was therefore of considerable interest to compare the nitric acid method with the manufacture of Nitroammophoska.

The solutions obtained under the usual conditions (Table 1) of the nitric acid decomposition of phosphates contain virtually the entire P_2O_5 and CaO from the starting material. In the processing of the Khibinsk apatite concentrate, the $CaO : P_2O_5$ weight ratio in the solutions is 1.3 and in the decomposition of the Karatau phosphorite it is about 1.6.

Complex fertilizers from nitric acid–phosphoric acid solutions (Nitrophos and Nitrophoska) are also obtained by their neutralisation with ammonia. Depending on the amount of ammonia introduced and on the calcium content in solution, the phosphate in the fertilizer can be present in water-soluble and citrate-soluble forms[43]. According to Eqn. (1), the nitric acid–phosphoric acid solution has the composition of $3H_3PO_4 + 5Ca(NO_3)_2$.

The theoretical compositions of the liquid and solid phase formed in the ammoniation of the nitric acid-phosphoric acid solutions could be determined beforehand by analysing the equilibrium five-component system $CaO-P_2O_5-N_2O_5-NH_3-H_2O$, which has been investigated in detail at 25°C and partly at 50°C.[44] This analysis has not been published but the experimental data are available,[7,43]. In order to obtain the bulk of P_2O_5 in a water-soluble form, only the first hydrogen ion of phosphoric acid should be

neutralised in the initial solution:

$$3H_3PO_4 + 5Ca(NO_3)_2 + 3NH_3 = 1.5Ca(H_2PO_4)_2 + 3NH_4NO_3 + 3.5Ca(NO_3)_2. \quad (5)$$

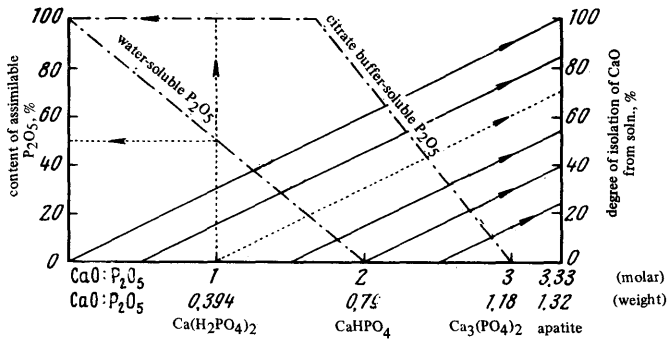


Figure 2. Dependence of the assimilable and water-soluble P_2O_5 content in Nitrophoska on the $CaO : P_2O_5$ ratio in the nitric acid–phosphoric acid solution from the apatite concentrate[47]; dashed line — example quoted for the $Ca : P_2O_5 = 0.394$ ratio.

Under these conditions, an appreciable amount of calcium nitrate remains in the reaction mixture, its presence impairing the physical properties (high hygroscopicity) of the fertilizer and reducing the concentration of nutrient materials in it. With increase of the degree of ammoniation, an increasing amount of P_2O_5 is converted into the citrate-soluble $CaHPO_4$:

$$3H_3PO_4 + 5Ca(NO_3)_2 + 6NH_3 = 3CaHPO_4 + 6NH_4NO_3 + 2Ca(NO_3)_2. \quad (6)$$

The preparation of $CaHPO_4$ for animal feed from nitric acid–phosphoric acid solution which had been freed from fluorine in a preliminary treatment is based on this reaction. The formation of $CaHPO_4$ for animal feed by the nitric acid decomposition of the apatite concentrate[45] and Karatau phosphorite[46] has been investigated.

In order to obtain Nitrophoska containing P_2O_5 partly or completely in a water-soluble form, the excess calcium must be removed from the nitric acid–phosphoric acid solution as far as possible (see the nomogram in Fig. 2).

The wide variety of methods for the binding of the excess calcium largely determine the nature of the nitrophosphate manufacturing processes. The characteristics of these processes are to a considerable extent reflected in their economic efficiency.

Two groups of methods for reducing the relative CaO content, which can be conventionally termed chemical and physicochemical, are known and widely employed. In recent years procedures of both these types have been considerably improved in the manufacture of nitrophosphates[48–60].

Among chemical methods, the nitric acid–carbonate method[49], characteristically requiring a preliminary complete ammoniation of the solution associated with the precipitation of the citrate-soluble $CaHPO_4$ [see Eqn. (6)], has found limited application. Only after neutralisation of the solution to pH 4 is it treated with NH_3 and CO_2 in order to form calcium carbonate at pH 7–8:

$$Ca(NO_3)_2 + 2NH_3 + CO_2 + H_2O = CaCO_3 + 2NH_4NO_3. \quad (7)$$

The $CaHPO_4$ and $CaCO_3$ precipitates are not separated in the nitric acid–carbonate method and remain in the fertilizer. Therefore, Nitrophoska obtained by this procedure from the apatite concentrate contains only 35–37% of nutrient substances and has the unfavourable ratios $N : P_2O_5 : K_2O = 1 : 0.7 : 1$.

Nitrophos from Karatau phosphorite contains up to 28.5% of nutrient substances and has the ratio $N : P_2O_5 = 1 : 0.6$. The entire P_2O_5 in the fertilizer is in the citrate-soluble formed. The comparatively low grade of the fertilizer and the inadequately balanced ratio of nutrient substances explain why this method has not become very common, despite its relatively favourable technical and economic characteristics.

Several procedures for the binding of calcium oxide by sulphate ions [sic] forming the sparingly soluble calcium sulphate, also belong to the class of chemical methods. Sulphate ions are introduced with sulphuric acid (the nitric acid–sulphuric acid method) with ammonium or potassium sulphate (the nitric acid–sulphate methods), and sometimes simultaneously with sulphates and with sulphuric acid.

In the preparation of Nitrophoska with 50% of P_2O_5 in a water-soluble form by the nitric–sulphuric acid method, theoretically only 30% of fluoroapatite is decomposed by nitric acid, the remainder reacting with sulphuric acid:

$$Ca_5(PO_4)_3F + 3HNO_3 + 3.5H_2SO_4 + 7H_2O = 3H_3PO_4 + 1.5Ca(NO_3)_2 + 3.5CaSO_4 \cdot 2H_2O + HF. \quad (8)$$

The neutralisation of the solution to pH 3.2 (at 80–100°C) proceeds according to equation

$$3H_3PO_4 + 1.5Ca(NO_3)_2 + 4.5NH_3 = 1.5CaHPO_4 + 1.5NH_4H_2PO_4 + 3NH_4NO_3. \quad (9)$$

It follows from Eqn. (9) that the amount of the water-soluble and citrate-soluble P_2O_5 in the product is 50% each. Under industrial conditions Nitrophoska is obtained with P_2O_5 which is assimilable (in the water- and citrate-soluble forms) to the extent of about 90%, of which up to 50% is in a water-soluble form.

According to Eqn. (9), the $N : P_2O_5$ ratio in the neutralised solution is 1 : 2 and therefore, in order to obtain a balanced fertilizer of the 1 : 1 grade, one introduces more than twice the amount of nitric acid required according to Eqn. (8). In practice the consumption of nitric acid per unit of nutrient substances does not differ from that in processes without the use of sulphuric acid, i.e. in fact sulphuric acid is consumed in the method described only in the binding of part of CaO and increases the cost of the raw material component.

Another important feature of the sulphuric acid method is that the calcium sulphate precipitate is not separated from the solution owing to its fairly unfavourable crystal structure and remains in the product. Consequently the concentration of Nitrophoska does not exceed 34–35% of the sum of nutrient substances. This procedure has been applied on an industrial scale in the USSR.

The above disadvantages have so far hindered a wide-scale application of the nitric acid–sulphuric acid method in world industry. In recent years the sulphuric acid method has been greatly improved[61,62] — it has been found that comparatively large readily filtered gypsum crystals are formed when part of the final solution returning to the process in order to dilute the reaction mass is circulated. This procedure makes it possible to include in the manufacturing scheme for sulphuric acid Nitrophoska the filtration and washing of the gypsum, as a result of which its concentration of nutrient substances can be increased to 50–51% for a fertilizer of the $N : P_2P_5 : K_2O = 1 : 1 : 1$ grade.

A version of the above scheme with replacement of

part of the sulphuric acid by ammonium sulphate was also investigated. The circulation scheme has been proved on an experimental industrial apparatus. The increased cost of the raw material, compared with other methods, persists in the circulation scheme but the improvements can enhance the efficiency of the present apparatus operating in accordance with the nitric acid–sulphuric acid procedure.

The nitric acid–sulphate method, in which a 40% solution of ammonium sulphate is used to bind the excess calcium (see Fig. 3), has found a relatively wider application in world industry[63,64]:

$$3H_3PO_4 + 5Ca(NO_3)_2 + 5(NH_4)_2SO_4 + 3NH_3 + 10H_2O = 3NH_4H_2PO_4 + 10NH_4NO_3 + 5CaSO_4 \cdot 2H_2O. \quad (10)$$

In this method the precipitated calcium sulphate is filtered off and converted by treatment with ammonium carbonate solution:

$$CaSO_4 + 2NH_3 + CO_2 + H_2O = (NH_4)_2SO_4 + CaCO_3. \quad (11)$$

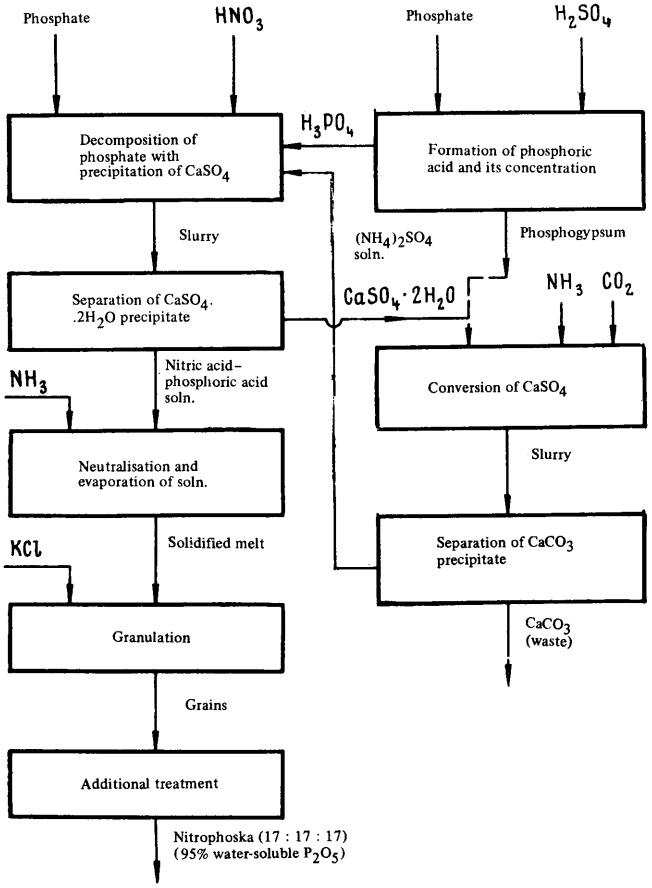


Figure 3. Fundamental scheme of the nitric acid–sulphate method for the manufacture of Nitrophoska.

The calcium carbonate precipitate is a side product and the ammonium sulphate solution formed is returned to the process The advantages of this method include the preparation of concentrated Nitrophoska in which the content of the total nutrient substances for the 1 : 1 : 1 grade is up to 51% and about 95% of P_2O_5 is in a water-soluble form.

The precipitation of calcium oxide requires the introduction of an amount of ammonium sulphate for which the $N : P_2O_5$ ratio decreases to 1 : 0.66. Thus, in order to obtain a more balanced product with the $N : P_2O_5 = 1 : 1$ ratio, it is necessary to introduce additional phosphoric acid, i.e. in this case sulphuric acid is also indirectly involved in the manufacture of Nitrophoska via the preparation of phosphoric acid by extraction.

A version has been developed, which provides for the additional introduction of sulphuric acid (together with nitric acid and ammonium sulphate solution) to decompose the phosphate, in an amount necessary to form phosphoric acid which balances the large amount of nitrogen introduced with ammonium sulphate[65].

The indirect or direct introduction of sulphuric acid into the process lowers the economic efficiency of the nitric acid method of manufacture of complex fertilizers, effectively reducing the amount of the cheapest P_2O_5 introduced in the form of natural phosphates. This version can be applied using the ammonium sulphate solution obtained as a side product in the manufacture of caprolactam.

Among the chemical methods in the next group, mention should be made of the nitric acid – phosphoric acid process based on the decrease of the $CaO : P_2O_5$ ratio in the nitric acid–phosphoric acid solution by the addition of phosphoric acid[66,67]. The process essentially differs little from the nitric acid–sulphuric acid process, since in the latter case sulphuric acid is also indirectly involved in the reaction whereby phosphoric acid is produced by extraction with formation of gypsum as waste.

Complex ternary fertilizers are usually manufactured from the commonest and cheapest potassium raw material–potassium chloride. Studies have been made on the nitric acid processing of phosphates (mainly Karatau phosphorites) also using potassium sulphate[68].

The manufacture of chlorine-free Nitrophoska is of great importance for the cultivation of many agricultural crops, the quality of which is adversely affected by the presence of chloride ions in the fertilizer. A characteristic feature of chlorine-free Nitrophoska is an enhanced content of K_2O: a product with the approximate ratios of 1 : 1 : 1.5 is obtained: the relative amount of water-soluble P_2O_5 does not exceed 50%.

The usefulness of the industrial process with introduction of potassium sulphate depends on the scale of the manufacture of potassium sulphate salts and also on the requirement for a complex fertilizer with an enhanced K_2O content. However, until recently the use of K_2SO_4 was impeded by the small scale of the manufacture of this salt.

High-grade chlorine-free Nitrophoska can be obtained by introducing potassium in the form of the carbonate (with separation of calcium carbonate) or the hydroxide (studies on the technology of the manufacture of Nitrophoska using these reagents are desirable).

The group of physicochemical methods for the reduction of the CaO content in nitric acid–phosphoric acid solutions includes the polythermal crystallisation of calcium nitrate, i.e. by reducing its solubility in the $CaO–P_2O_5–N_2O_5–H_2O$ system on lowering the temperature. This system has been inadequately investigated at temperatures below 0°C, so that the so called "freezing out" of calcium nitrate has been investigated mainly empirically under the conditions of the technological process[7,48,69]. It was shown

that the degree of precipitation of calcium nitrate tetrahydrate and hence the content of water-soluble P_2O_5 in the fertilizer (for nitric acid concentrations in the range 47 to 55% and amounts of nitric acid up to 140% of stoichiometry) depend on temperature (in the range from -15° to +20°C). With increase of the concentration and amount of nitric acid and with decrease of solution temperature, the yield of calcium nitrate and the content of water-soluble P_2O_5 in the product increase (Fig. 4).

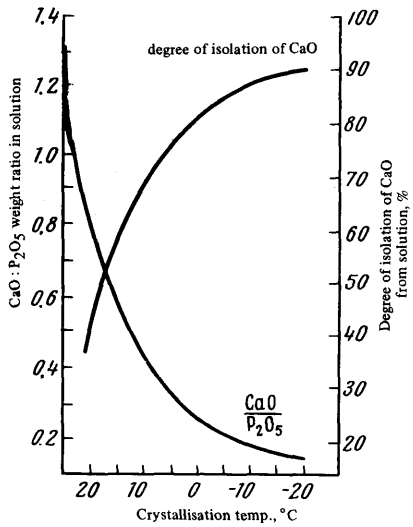


Figure 4. Temperature variation of the degree of isolation of CaO from the nitric acid–phosphoric acid solution (in the decomposition of the apatite concentrate with nitric acid at a concentration of 56–58%)[70].

In the application of the process on an industrial scale with separation of calcium nitrate by cooling, certain technical difficulties were encountered, which delayed the wide scale application of this method. The point is that calcium nitrate tetrahydrate can form an encrustation on the cooled surface of the crystalliser, gradually decreasing the heat transfer coefficient, i.e. increasing the energy expenditure on cooling.

The initial proposals[71,72] for the manufacture of Nitrophoska by the cooling method provided for the formation of the fertilizer with up to 40% of water-soluble P_2O_5 and the simultaneous manufacture of a second product – calcium nitrate (a nitrogen fertilizer containing 15.5% of nitrogen).

The manufacture of Nitrophoska with cooling of the solution to +10°C by the method of Vol'fkovich and Loginova[72] was tested in the USSR on an experimental industrial scale at a nitrogen fertilizer factory, where studies were also made on the nitric acid–carbonate and nitric acid–sulphate methods[39].

The method using polythermal crystallisation of calcium nitrate emphasises the principle of using nitric acid alone for the decomposition of phosphate with simultaneous introduction into the product of nitrogen as a nutrient element.

For the economics of the procedure, it is also important that the entire P_2O_5 enters the process only as the natural phosphate, i.e. in the cheapest form.

The potential economic efficiency of the method with cooling promoted the development of many improvements to the technological process. In recent years multistage cooling (to -5°C) of the slurry obtained in the decomposition of the phosphate raw material with nitric acid (58 to 60%) was used in several countries. The crystallisers are gradually filled and unloaded, so that a continuous flow of the cooled pulp is achieved. This ensured the formation of a coarsely crystalline calcium nitrate, which is readily separated from the mother liquor on filters and in centrifuges. After the additional treatment of the mother liquor, it is possible to obtain Nitrophoska of the 1 : 1 : 1 grade containing about 50% of the total nutrient substances. The amount of P_2O_5 assimilated in the product reaches 96%, including 80–85% of water-soluble P_2O_5.[73–77]

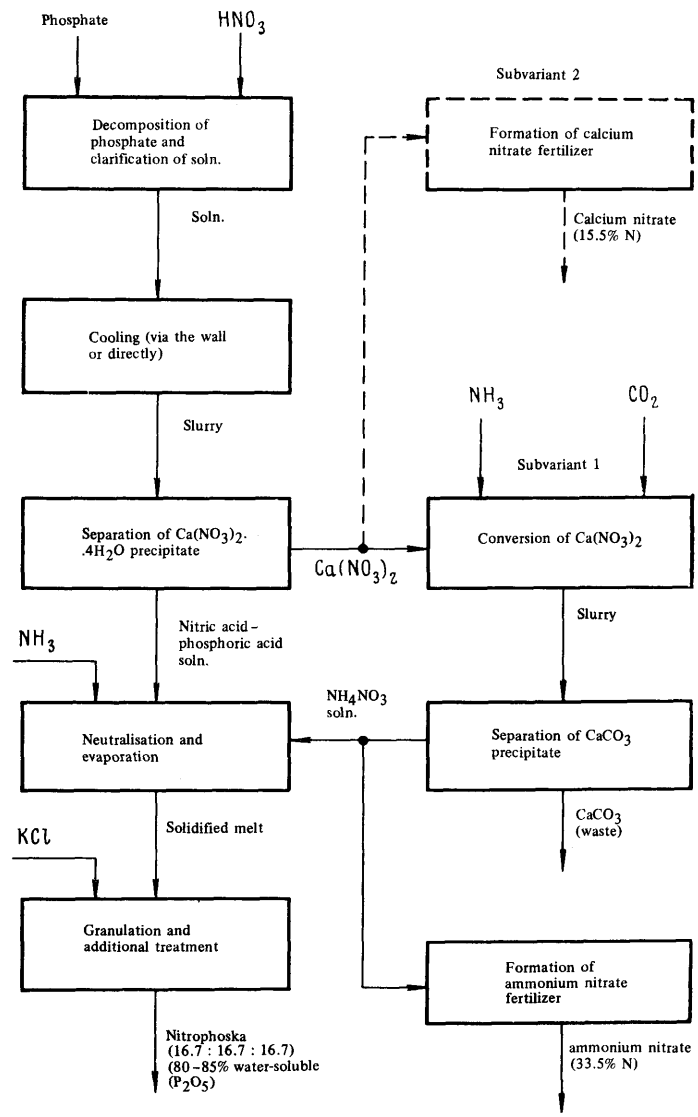


Figure 5. Fundamental scheme of the manufacture of Nitrophoska by the method with polythermal crystallisation of calcium nitrate.

The conversion of the ammoniated mother liquor into the solid fertilizer was also improved and the conversion of the calcium nitrate tetrahydrate isolated into ammonium nitrate [see Eqn. (4)] was introduced. The 95% ammonium nitrate solution can be added in different amounts to the mother liquor in order to maintain the specified $N:P_2O_5$ ratio in Nitrophoska. The remaining ammonium nitrate is issued as a second product — a nitrogen fertilizer with 34% of nitrogen (Fig. 5).

The conversion of calcium nitrate yields a side product (calcium carbonate), which can be used in agriculture for the impregnation of soils with lime and in many manufacturing processes: in the formation of $CaHPO_4$, $Ca(H_2PO_4)_2$, etc. The weight of calcium carbonate is about 75% of that of calcium sulphate (calculated for the anhydrous form) produced in the manufacture of phosphoric acid by extraction for the same amount of phosphate raw material.

The comparatively low cost of the raw material, the satisfactory quality of the product, the possibility of altering the $N:P_2O_5$ ratio in the fertilizer without much difficulty, and the more satisfactory situation as regards industrial waste explains why the manufacture of Nitrophoska by the cooling method has expanded in many countries. During recent years, the output capacity of the existing factories and factories under construction for the manufacture of Nitrophoska by this method in Norway, German Federal Republic, Denmark, France, USA, and Romania reached 6 000 000 tons per year[77].

A further improvement of the cooling method was developed in Czechoslovakia[70,78]. It consists in the replacement of heat exchange via the cooled surface by direct removal of heat by the cooling liquid (for example white spirit), which is immiscible with the slurry The process is continuous, eliminating the encrustation of the cooled surfaces by calcium nitrate crystals. The energy expenditure on the cooling of the slurry is reduced by approximately 10%. This process has been adopted on an industrial scale.

Fig. 6 shows the dependence of the $N:P_2O_5$ ratio and the content of the citrate-soluble or water-soluble P_2O_5 in Nitrophoska obtained by the above method for different amounts of nitric acid used for the decomposition of the apatite concentrate[47]. The possibility of precipitating part of the calcium nitrate as the anhydrous salt directly in the decomposition of natural phosphates with concentrated (80%) nitric acid at a temperature of the order of 60°C has been established experimentally[18,19]. The amount of calcium nitrate isolated makes it possible to obtain Nitrophoska containing up to 80% of P_2O_5 in the water-soluble form. The scheme of the technological process developed on the basis of these studies is close to the usual scheme for sulphuric acid extraction. The development of a modern technology for the concentration of nitric acid makes this process for the manufacture of Nitrophoska very promising. It is useful to continue this study of the process on an experimental industrial scale.

A new trend has arisen in the conversion of nitric acid–phosphoric acid solutions into fertilizers by extracting phosphoric and nitric acids with organic solvents[79]. One of these methods[80-83] consists of extraction with t-pentyl alcohol. The washed organic phase is neutralised with ammonia. On standing, the extract separates into the pure organic solvent and an aqueous slurry containing ammonium nitrate and phosphates. After evaporation and addition of potassium chloride, Nitrophoska of 18 : 18 : 18 grade is obtained.

For the complete isolation of calcium nitrate, the organic phase is washed with a solution of ammonium nitrate. The resulting aqueous phase together with the wash solution is treated with ammonium carbonate to convert calcium nitrate into ammonium nitrate [see Eqn. (4)]. The method has not yet found wide scale application in industry.

A further procedure of this kind has been developed, in which isobutyl alcohol is used as the organic solvent[84-86]. The final products are ammonium dihydrogen phosphate and ammonium nitrate and the waste is calcium carbonate. The method has been applied on an experimental industrial apparatus.

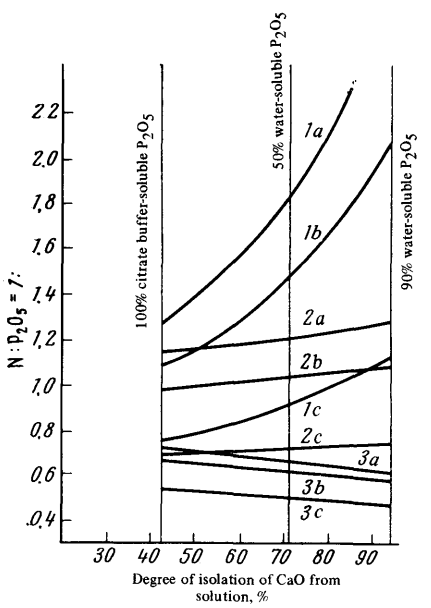


Figure 6. Variation of the $N:P_2O_5$ ratio with the degree of isolation of CaO from the nitric acid–phosphoric acid solution in the decomposition of the apatite concentrate with nitric acid[47]: *1*) method with cooling, no recycling ammonium nitrate; *2*) nitric acid–sulphuric acid method; *3*) nitric acid–sulphate method, without recycling of ammonium sulphate and method with cooling and with recycling of ammonium nitrate; percentage of nitric acid relative to the stoichiometric amount required to decompose the apatite; *a*) 100; *b*) 110; *c*) 140.

Another new trend in the nitric acid processing of phosphates is associated with the use of carbamide[87-90]. Its importance is that carbamide, which forms the readily soluble carbamide phosphate $CO(NH_2)_2.H_3PO_4$ and binds calcium nitrate in the complex $Ca(NO_3)_2.4CO(NH_2)_2$, makes it possible to obtain fertilizers with a high proportion of P_2O_5 in the water-soluble form with a smaller amount, than in other procedures, of calcium isolated from the nitric acid–phosphoric acid solution. It would be useful to investigate further the nitric acid processing of phosphates using carbamide in order to develop effective versions of the manufacturing process for concentrated and balanced water-soluble nitrophosphates.

The preparation of the nitric acid–phosphoric acid solutions for subsequent conversion into fertilizers is not exhausted by the procedures enumerated above. Other versions and methods have been proposed and investigated.

IV. CONVERSION OF AMMONIATED SOLUTIONS INTO SOLID FERTILIZERS

The concluding stages of the processing of the solutions include a number of operations such as the isolation of water (by evaporation or drying), granulation with addition of potassium salts, conditioning (cooling, screening, powdering, librication, encapsulation, pressing, and others). These operations depend to only a slight extent on the methods of preparation of the solutions and therefore different types of apparatus may be employed regardless of the methods used to decrease the relative amount of calcium and for the ammoniation process.

The ammoniated slurry is granulated under industrial conditions with recycling and simultaneous drying of the product in a drum drier ("spherodiser") or in a drum granulator-drier in the industrial application of the nitric acid–sulphuric acid, nitric acid–sulphate, and nitric acid–phosporic acid methods. Such apparatus for the isolation of water and granulation does not use the heat of neutralisation of the acid and therefore entails a high energy expenditure.

The nitric acid–phosphoric acid method is also employed with preliminary neutralisation of the ammoniating-granulating solution and drying of the product in a drum drier. In this version the heat of neutralisation is largely used for the removal of water.

Numerous varieties of industrial apparatus are used to evaporate the neutralised solutions until the formation of a solidified melt and to granulate the latter in spray towers without additional drying of the product. Abroad this process is termed "prilling". The advantage of this method consists in a minimal energy expenditure.

In other schemes neutralised solutions are also evaporated and then granulated in a blade granulator with recycling and subsequent drum drying of the product. Certain companies outside the Soviet Union employ also a different variety of apparatus for technological processes which are essentially of the same type.

V. COMPARATIVE ANALYSIS OF TECHNOLOGICAL PROCESSES IN THE MANUFACTURE OF COMPLEX FERTILIZERS

In the manufacture of complex fertilizers by modern methods 76–87% of the cost is represented by that of the raw materials. The consumption and quality of the raw material are therefore important factors, which reflect the economic efficiency of the methods of manufacture.

For all types of complex fertilizers of the same grade, the consumption of N, P_2O_5, and K_2O is virtually identical: for example, for fertilizers with the $N:P_2O_5:K_2O = 1:1:1$ ratios, it amounts to 0.33–0.35 tons per ton of each nutrient substance. However, the unit costs of nitrogen and P_2O_5 in different raw materials are not the same. The cheapest types of raw material are synthetic ammonia and natural phosphates (apatite and phosphorite concentrates). Therefore, the method of manufacture of a complex fertilizer which requires the cheapest raw materials containing nitrogen and phosphorus will be economically the most efficient ‡.

Comparison of the technological processes used to manufacture complex fertilizers shows[91] that the relative consumption of nitrogen introduced with ammonia (synthetic ammonia or ammonium sulphate) and nitric acid is virtually the same for all the methods considered here. The amount of ammonia nitrogen is in the range 57–62% and that of the nitrogen introduced with nitric acid is 43–38%.

All the methods for the manufacture of both Nitroammophoska and Nitrophoska involve the additional consumption of sulphuric acid (directly or in the manufacture of phosphoric acid). The only exception is the manufacture of Nitrophoska with isolation of calcium nitrate by cooling. The cooling method differs from all others for the synthesis of complex fertilizers also by the fact that the entire P_2O_5 is introduced in the cheapest form — as the natural phosphate. In other words the decomposition of the phosphate raw material in this method is achieved with nitric acid alone, without the additional consumption of sulphuric or phosphoric acid.

The above analysis leads to the conclusion that the cost of the manufacture of Nitroammophoska by treatment with phosphoric and nitric acids and also of Nitrophoska by the nitric acid–sulphuric acid and nitric acid–phosphoric acid methods is highest. The nitric acid–sulphate methods occupy an intermediate position and the manufacture of Nitrophoska by procedures involving the isolation of calcium nitrate by cooling should be least expensive. This conclusion is confirmed by the finding that in the last manufacturing process moderate cooling is employed: a temperature from +10° to -10°C, which can be achieved by combination with the synthesis of ammonia involving a relatively low energy expenditure.

The above data disprove the common view expressed by some investigators[92,93] that the manufacture of Nitrophoska can be useful only provided that the reserves of sulphur in the country are limited or when the sulphur-containing raw material is expensive. However, in fact the cooling method permits economically efficient processing of the phosphate raw material without any consumption of sulphur, using the same amount of nitric acid as in other methods for the manufacture of Nitrophoska — a complex fertilizer.

Approximate calculations of the intrinsic unit cost of the nutrient substances obtained by different methods confirm the above conclusions[52,53,58,91,94–96].

When calcium nitrate is manufactured as a commercial by-product, the manufacture of Nitrophoska by the cooling method takes place without waste. The conversion of calcium nitrate into ammonium nitrate makes it possible to obtain calcium carbonate as a by-product. Compared with the methods for the manufacture of complex fertilizers involving the formation of calcium sulphate as waste, the formation of calcium carbonate simplifies and reduces the cost of the employment of the calcium waste.

The determination of the capital costs is important for the assessment of the different methods of manufacturing complex fertilizers. In certain published studies[94,96] the specific capital investment with the associated cost of the manufacture of Nitrophoska by the cooling method is lower than in the manufacture of Nitroammophoska, while in the manufacture by other procedures[95] the costs are at approximately the same level.

Analysis of the present development of the technology of the nitric acid processing of natural phosphates shows that the method with polythermal crystallisation of calcium nitrate and conversion of the latter into ammonium nitrate or without conversion is promising.

The main advantages of the process with cooling are the lowest cost of the raw material in consequence of the

‡ Since regardless of the method of manufacture, potassium is in most cases introduced as the chloride, its cost does not affect the comparative assessment of the manufacture of complex fertilizers.

effective processing of the cheapest phosphate raw material without the consumption of sulphuric or phosphoric acid, the possibility of obtaining complex fertilizers of different grades on the same apparatus without significant changes in the technological process, and the formation of calcium carbonate as the by-product instead of calcium sulphate (when calcium nitrate is converted into ammonium nitrate).

Studies on new technological processes for the manufacture of complex fertilizers retaining the basic and fruitful idea of employing nitric acid for the decomposition of natural phosphates without the addition of other acids or their salts are useful and merit support.

It is clear from the foregoing that the processes involving the conversion of natural phosphates by nitric acid into complex fertilizers have greatly developed in recent years both in terms of scale and the wide variety of chemical-engineering manufacturing schemes and as regards their more detailed physicochemical investigation. These processes are of great interest and promise and they have been investigated both theoretically and technically to an extent sufficient for the selection of the optimal scheme for the manufacture of Nitrophoska with polythermal crystallisation of calcium nitrate, meeting the highest technical and economic requirements among all other known methods for the synthesis of complex fertilizers.

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