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I

A vast majority of USSR soils and agricultural crops require both phosphorus and nitrogen fertilizers. For this reason the economically expedient combination of phosphate and nitrogenous fertilizers production into a single technological process is of great interest.

Until recently, only ammonia was used in the production of phospho-nitrogenous fertilizers. Nitric acid began to come into use for ~~solution~~ decomposition of phosphate in the foreign fertilizer industry only a few years ago, a result of large-scale expansion of the industrial ammonia synthesis and oxidation to nitric acid, which became considerably cheaper as a result.

The main advantage of the nitric acid process for ~~dissolving~~ decomposing phosphates over the use of sulphuric and hydrochloric acids for the same purpose lies in the virtually complete, complex utilization of the reacting masses, accompanied by utilization of the energy of nitric acid to dissolve phosphorite. When

H_3PO_4 and concentrated phosphate fertilizers are produced with H_2SO_4, phosphogypsum, which is not ~~un~~utilized or only slightly utilized, is produced; when HCl is used, $CaCl_2$ is formed, and this is also not ~~un~~utilized; that is, these processes only utilize the chemical energy of these acids, without their appearing in the end products. When nitric acid is used instead for dissolution, not only is its chemical energy utilized; it also appears in the product -- fertilizer -- in the form of $Ca(NO_3)_2$.

The nitric acid process further allows the expedient use of fluorine (according to work done by M. Dornish, M. Sladkovaya, A. Polyak and others); when Khibinsk apatite is processed rare earths may also be used efficiently. These materials are very necessary and valuable to the national economy.

In view of the vast scale of the fertilizer industry, the decomposition ~~dissolution~~ of phosphates by nitric acid would permit the assimilation of great quantities of HNO_3.

Despite the great interest in the nitric acid method displayed by major foreign cartels and manufacturers these methods have still not been widely adopted. Only three or four relatively small plants have been built in various countries during the past few years (using various technological systems). This is apparently due, on the one hand, to results of economic crisis and depression in the capitalist countries, and on the other hand, is explained by the technical difficulties of mastering this technological method.

In view of the lack of foreign literature throwing light on the technology of phosphate dissolution by nitric acid (except for the numerous patents) and in view of the number of technical difficulties which arise when these methods are tried out for checking purposes, the Scientific-Research Institute for Fertilizers, Insecticides and Fungicides (NIUIF) has in recent years been carrying on an extensive series of laboratory experiments, and, to some extent, pilot-plant operations with various types of raw materials; it has also made agronomic tests and technical and economic computations as to the expediency of this technological approach relative to others.

The following institutions have also worked in the same field (starting earlier): The Institute of General and Inorganic Chemistry of the Academy of Sciences USSR; the Ukrainian Affiliate of the NIUIF; the Belorussian Industrial Institute; the Central Laboratory of the Chernoreka Plant; the GIPROAZOT, and others.

The main difficulties and failings of the nitric acid method (many of which have already been overcome) consist of aggravated corrosion of plant equipment, considerable loss of nitrogen in the dissolution of phosphorites of organic origin (which losses it has proved possible to stop by elimination of organic matter and oxidation of the ferrous compounds through roasting the phosphorites); hygroscopicity of the end product by reason of its $Ca(NO_3)_2$ or NH_4NO_3 content (which can be reduced by separation of the reaction products, by mixing with potassium or other metal salts, by granulating them, or by other methods);

the difficulty of filtering and decanting the intermediate products when phosphorites of organic origin are processed (roasting, elimination of fluorine and silica by means of alkaline salts, and other measures) have almost entirely eliminated this difficulty.

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II

There are a number of variations of ~~nitric acid~~ phosphorite ~~dissolution.~~ decomposition with nitric acid The ones deserving the greatest attention from ~~is expressed in~~ the ~~following~~ technological ~~cycle:~~ standpoint ~~is~~ are expressed by the following formulas:

(a) $Ca_3P_2O_8$ Rest + $4HNO_3$ = $CaH_4(PO_4)_2$ + $2Ca(NO_3)_2$ + Rest, (1)

where Rest represents ~~the~~ other constituents of the phosphate rock, including the undissolved residues.

What we have in mind is a process not involving the separation of the products of reaction.

As a result of this process, which recalls the production of superphosphate, a heavy, comparatively low-grade product is obtained, containing all the constituents of the original phosphate rock, P_2O_5 in water-soluble form, and nitrogen as $Ca(NO_3)_2$.

(b) ~~Dissolution~~ Decomposition according to the equation

$$Ca_3P_2O_8 \text{ Rest} + 6HNO_3 = 3Ca(NO_3)_2 + 2H_3PO_4 + \text{Rest} \qquad (2)$$

followed by separation by means of decantation or filtration of the H_3PO_4 and $Ca(NO_3)_2$ solution from the insoluble residue.

This operation is not essential if the insoluble residue is very slight (as with flotation apatite). As a result of the complete neutralization of the H_3PO_4 by any base, either a complex nitrogen-phosphorus fertilizer or separate phosphate and nitrogenous fertilizers may be obtained in this variant.

Production of nitrosuperphosphate was accomplished a few years ago on the pilot-plant scale in Switzerland (De-Lon~~gue~~za), but in view of a number of disadvantages, this method has not yet been adopted elsewhere. At various times this process has been studied in the NIUIF by different research workers -- S. Vol'fkovich, M. Golitsina, L. Berlin, L. Gurevich, L. Goritskaya, and R. Yakobson. An advantage of this method is the simplicity of the process. Since the product obtained, however, is low-grade and very hygroscopic (even when ~~driers are added in the course~~ drying is introduced into the process of manufacture, or when the return product is chilled) and requires special storage conditions and special packing or mixture with other fertilizers, the USSR is not contemplating production.

Many authors have proposed the ~~dissolution~~ decomposition of phosphates according to equation (2), with subsequent neutralization of the acid solution by means of CaO or $CaCO_3$, NH_3 or $NH_4(CO_3)$, or ammoniates instead of ~~dissolution~~ decomposition by H_2SO_4, $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, $NaNO_3$, KNO_3, or other reagents (either singly or together). A number of these schemes have been studied in the NIUIF. ✓

The advantage of these schemes is the production of a higher-grade fertilizer than nitrosuperphosphate; their disadvantage is the great complexity of the technological processes involved.

Study of the production of so-called ammonitrophos, which is characterized by the processing of a nitric and phosphoric acid extract (without filtration of the undissolved residues from the ammonia and carbonic acid) has not, up to the present, shown any positive results. In this method, the calcium phosphates are precipitated as residues (mostly in citrate-soluble form) together with calcium carbonate and the undissolved residue, while ammonium nitrate remains in solution. The product contains a dried and ground mixture of all these salts. The difficulty of drying the product, its high capacity for absorbing moisture, and primarily the considerably lower availability for plant assimilation of the P_2O_5 in ammonitrophos as compared with that in $CaHPO_4$ have joined to make these schemes of production unacceptable up to now. (See papers by S. Vol'fkovich, L. Antokhinaya, A. Bun'kovaya, I. Mirkin, A. Loginovaya, A. Polyak, L. Grinshpan, N. Blagoveshchenskaya, S. Kaluginaya and others.)

The production of $CaHPO_4$ and $Ca(NO_3)_2$ based on the neutralization of the H_3PO_4 in a mixture with $Ca(NO_3)_2$ is the simplest method and the one that is most highly developed at present. It is used in one foreign plant and is scheduled to be employed in the USSR. Its basic disadvantage is its hygroscopicity and low concentration of $Ca(NO_3)_2$ in comparison with the method described below, and the fact that the P_2O_5 it contains is in citrate-soluble (but not water-soluble) form.

A. I. Loginovaya of the NIUIF has studied the production of $NH_4(NO_3)_2$ and $NH_4H_2PO_4$ based on the separation of H_3PO_4 and $Ca(NO_3)_2$ -- the calcium by means of $(NH_4)_2SO_4$, followed by neutralization of the solution with NH_3 and regeneration of the phosphogypsum obtained by use of ammonium carbonate. A process having a similar technological system is in use at one foreign plant. Its advantage is the possibility of securing a highly concentrated fertilizer -- ammophos with ammonium nitrate -- while its main disadvantages are the complexity and awkwardness of the technological process.

Other variants of this process employing Na_2SO_4, K_2SO_4, K_2CO_3, and other reagents have been tested, so far only for purposes of general orientation.

Among the new variants the method proposed by A. Belopol'skiy for obtaining not $CaHPO_4$ but $CaH_4(PO_4)_2$ from the nitric-phosphoric acid extract by neutralizing it with lime is deserving of serious consideration. This proposal is the result of an investigation into the physical chemistry of the equilibrium of the system $CaO - P_2O_5 - N_2O_5 - H_2O$ at 50 degrees and 25 degrees, and is being studied at the present time.

Below we give short descriptions and characteristics of two technological systems which have been most thoroughly studied and have the greatest practical interest from our point of view.

METHOD OF DERIVING $CaHPO_4$ AND $Ca(NO_3)_2$

This process was studied in detail on flotation apatite through an extensive laboratory research project carried out in 1935 by the NIUIF, and the basic coefficients needed for the formulation of plans for a plant were obtained.

The process can be divided into three basic elements:

(a) dissolution of flotation apatite by means of nitric acid;

(b) processing of the solutions obtained from that dissolution to precipitate out the phosphoric acid;

(c) evaporation or further processing of the calcium nitrate solutions.

This process is characterized by the following basic equations:

$$Ca_5(PO_4)_3F + 10HNO_3 \rightarrow 5Ca(NO_3)_2 + 3H_3PO_4 + HF.$$

The hydrofluoric acid reacts with the silica, which is always associated in small quantities with flotation apatite, according to the equation

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O.$$

The project brought out the necessity of separating out the SiF_6'' to obtain a precipitate with satisfactory physical properties (readily filtrable and washable). This separation was accomplished by precipitating it out as Na_2SiF_6 by means of sodium nitrate according to the formula

$$H_2SiF_6 + 2NaNO_3 \rightarrow 2HNO_3 + Na_2SiF_6.$$

The coefficient of precipitation of the fluorine by this method amounted to 80 to 85 percent.

This silicon fluoride precipitation yields as a by-product a salt that can be used as an insecticide.

The precipitation of the solutions after the nitric acid dissolution of the flotation apatite may be done with either lime (milk of lime) or limestone.

Precipitation by lime proceeds according to the equation

$$Ca(OH)_2 + H_3PO_4 + Ca(NO_3)_2 + aq \rightarrow CaHPO_4 + Ca(NO_3)_2 + aq.$$

The residual H_2SiF_6 and Na_2SiF_6 are hydrolyzed with the formation of colloidal forms of calcium fluoride and silica:

$$H_2SiF_6 + 3Ca(OH)_2 \rightarrow 4H_2O + SiO_2\downarrow + 3CaF_2\downarrow.$$

The sesquioxides are precipitated as phosphates:

$$2R(NO_3)_3 + 2H_3PO + 3Ca(OH)_2 \rightarrow 3Ca(NO_3)_2 + 3H_2Q + 2RPO_4\downarrow.$$

If the acid solution is precipitated by limestone (calcium carbonate) instead, the following reactions take place:

(1) $H_3PO_4 + Ca(NO_3)_2 + CaCO_3 + aq \rightarrow CaHPO_4\downarrow + Ca(NO_3)_2 + aq + CO_2\uparrow.$

(2) $CaCO_3 + H_2SiF_6 \rightarrow CaSiF_6 + H_2O + CO_2.$

(3) $2R(NO_3)_3 + 2H_3PO_4 + 3CaCO_3 \rightarrow 2RPO_4 + 3Ca(NO_3)_2 + 3CO_2 + aq...$

No hydrolysis of the residual Na_2SiF_6 takes place.

Comparison of the precipitations by lime and limestone dictated preference be given the latter, since the precipitate prepared from lime was considerably inferior in physical properties (crystalline structure, filtrability) and chemical properties (solubility in citrate-ammoniacal solution) to that obtained by limestone.

The coefficient of precipitation of P_2O_5 by limestone of the fineness of grind indicated reached a very high level -- 99 to 98 percent. This fact shows to advantage the precipitation of solutions obtained by flotation apatite dissolution with nitric acid from that of sulfuric acid extracts of apatite, and is apparently due to the buffer effect of $Ca(NO_3)_2$.

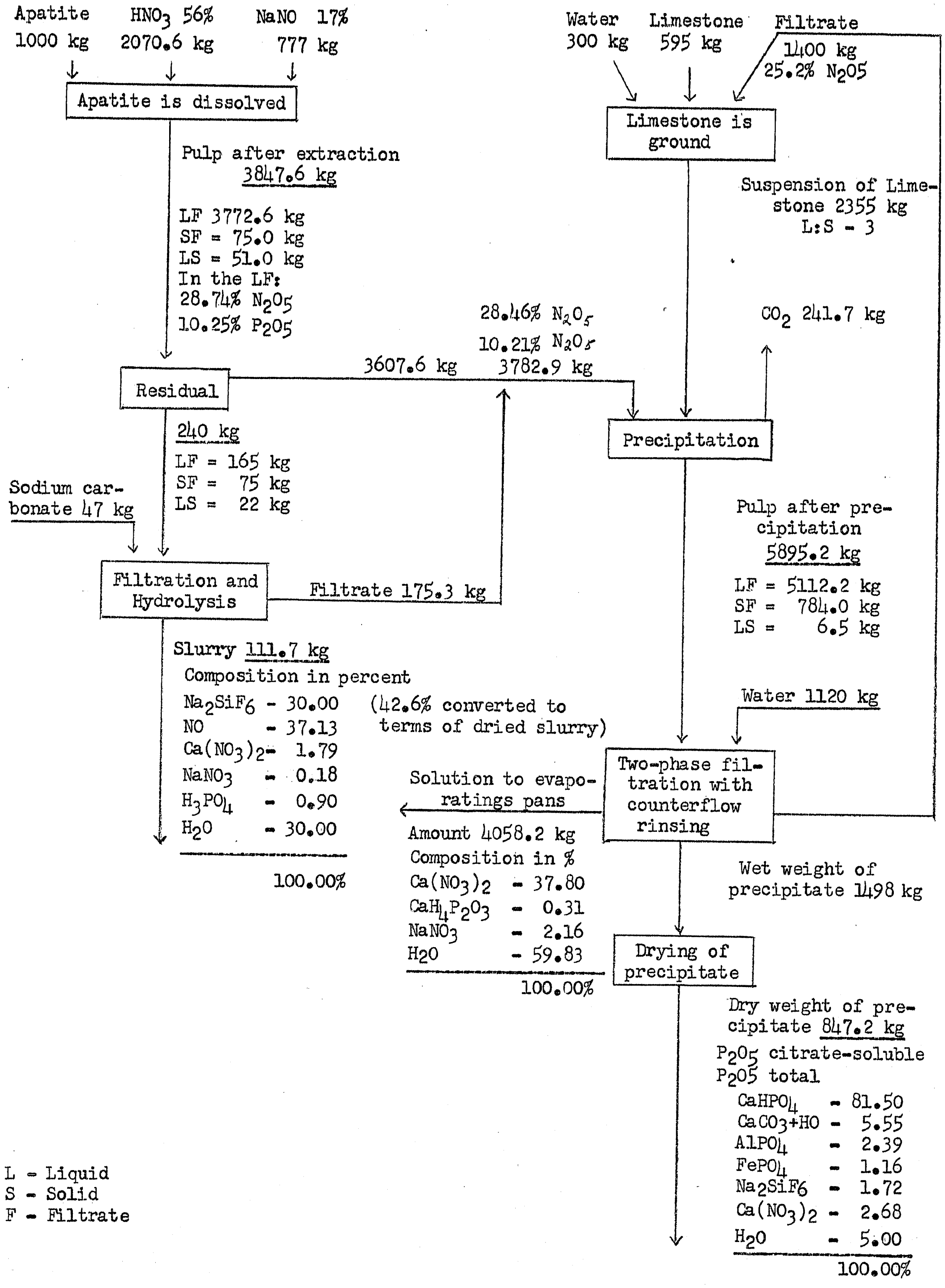

Figure 1. Material Balance Sheet of Production of Precipitate and Calcium Nitrate from Flotation Apatite, Nitric Acid and Limestone.

It has been demonstrated that it is possible to dry the precipitate obtained with limestone to a total moisture content of 5 percent without loss of citrate-solubility.

The conversion of calcium nitrate solutions to ammonium nitrate by precipitation with ammonium carbonate has been tested with the object of obtaining a fertilizer richer in nitrogen. The equation is as follows:

$$Ca(NO_3)_2 + (NH_4)_2CO_3 + aq \rightarrow CaCO_3 \downarrow + 2NH_4NO_3 + aq.$$

The test yielded wholly favorable results both as regards the coefficient of conversion (which was 100 percent) and the filtrability of the carbonate slurry.

Based on a large number of experiments, the industrial steps for the process have been formulated as shown in Figure 1.

Flotation apatite is dissolved with 55-percent nitric acid. During the process a 17 percent solution of $NaNO_3$ is introduced to precipitate out the H_2SiF_6 in the form of Na_2SiF_6. The solution is decanted to remove the undissolved residue of flotation apatite mixed with the precipitated sodium silicofluoride, which is washed free from the solution and either turned out as a finished product containing up to 42 percent Na_2SiF_6 (insecticide) or is further processed. Finely ground limestone is then added to the solution to induce a two-phase precipitation.

During the first stage of precipitation before the main precipitation occurs the rare earth phosphates separate out and the liquid is decanted to remove them.

The main precipitation occurs during the second stage. This precipitate consists of $CaHPO_4$, which is separated and washed free of remaining calcium nitrate solution by filtration through continuous-process drum filters, dried, and turned out as finished fertilizer. The $Ca(NO_3)_2$ solution is either evaporated to obtain a fertilizer or is further processed by conversion to ammonium nitrate through reaction with ammonium carbonate. Part of the calcium carbonate formed in the latter case is returned to the process for re-use in precipitation.

The consumption coefficients per 1,000 kilograms of flotation apatite are as follows: 55 percent nitric acid, 2,070 kilograms; sodium nitrate (in 17 percent solution), 777 kilograms; limestone (or calcium carbonate), 595 kilograms; water, 112 kilograms.

The yield per 1,000 kilograms flotation apatite is as follows:

Insecticide containing up to 42 percent Na_2SiF_6 -- 67 kilograms. (The quality of this product is subject to check on a pilot-plant scale.)

Precipitate containing 44.5 percent of assimilable P_2O_5 -- 847 kilograms.

Calcium nitrate (with admixture of 4.5 percent $NaNO_3$) -- 1,950 kilograms.

Rare earth phosphates (with content of 25 percent T/R_2O_3) -- 20 kilograms.

At present the laboratory and model tests of this method have been completed. The method may now be used as a basis of formulation of a project for construction of the first industrial plant.

III

METHOD OF DERIVING NH_4NO_3 AND $NH_4H_2PO_4$

This method was suggested in 1926 by S. I. Vol'fkovich and abroad by G. Lilienrot.

The method consists of treating with an ammonium sulfate solution the solution obtained by dissolving phosphate rock with nitric acid. After separation of the precipitated calcium sulfate, the solution is neutralized with ammonia to form monoammonium phosphate. The calcium sulfate is then converted by treatment with ammonia and carbonic acid (or ammonium carbonate) to ammonium sulfate.

The following are the basic equations for this process:

$$H_3PO + Ca(NO_3)_2 + (NH_4)_2SO_4 + 2H_2O \downarrow CaSO_4 \bullet 2H_2O + 2NH_4NO + H_3PO_4,$$

$$H_3PO_4 + NH_4NO_3 + NH_3 + H_2O \rightarrow NH_4H_2PO_4 + NH_4NO_3 + H_2O.$$

$$CaSO_4 \cdot 2H_2O + 2NH_3 + CO_2 \rightarrow (NH_4)_2SO_4 + CaCO_3 \downarrow + H_2O.$$

The conditions of separation of the rare earth from apatite were investigated in this paper. The latter may be separated as phosphates by neutralizing the solution of nitric and phosphoric acids with lime, ammonia or other alkali. With the separation of the rare earth the crystallization of the calcium sulfate improves, and then forms compact agglomerates.

The $H_3PO_4 + NH_4NO_3$ process solution is saturated with ammonia at 80 degrees, while the pH is slowly increased with rigid uniformity; this makes separation of the admixtures in the form of a crystalline precipitate possible.

The main reactions which take place while the solution is being saturated with ammonia up to pH = H follow:

$$H_3PO_4 + NH_4NO_3 + NH_3 + H_2O \rightarrow NH_4H_2PO_4 + NH_4NO_3. \quad (3)$$

$$R(NO_3)_3 + 2H_3PO_4 + 4NH_3 + aq \rightarrow RNH_4H_2(PO_4)_2 \downarrow + 3NH_4NO_3. \quad (4)$$

$$Ca(NO_3)_2 + H_3PO_4 + 2NH_4OH \rightarrow \downarrow CaHPO_4 + 2NH_4NO_3 + 2H_2O. \quad (5)$$

$$H_2SiF_6 + 8NH_3 + 4Ca(NO_3)_2 + 3H_2O \rightarrow \downarrow CaF_2 + \downarrow CaSiO_3 + 8NH_4NO_3. \quad (6)$$

When the CaO content in the liquid phase is in excess relative to the F and SiO_2, and all other conditions are unchanged, the crystallization of CaF_2, and especially of $CaSiO_3$, is improved. This may be explained by the passage of all the SiO_2 over into the molecular-disperse state under such conditions. Similarly favorable conditions are created if, as the reader has already been reminded, the greater part of the F and SiO_2 (70 percent) is separated from the solution in the form of Na_2SiF_6.

By evaporating the pulp (containing principally NH_4NO_3 and $NH_4H_2PO_4$) a fertilizer containing 15.5 percent P_2O_5 and 26.6 percent of N may be obtained. This fertilizer is in a state of disbalance in the ratio between its P_2O_5 and N contents (P_2O_5: N = 0.6:4), and it suffers from considerable hygroscopicity.

Therefore, it is more expedient to produce a separation of the mixture into NH_4NO_3 and $NH_4H_2PO_4$.

Such a separation is based on a reduction in the monoammonium phosphate solubility as the NH_4NO_3 concentration increases. At a concentration of 60 to 62 percent for the latter, and temperature of 20 degrees, 92 to 94 percent of the monoammonium phosphate is precipitated out. One method of separating out this mixture is by salting out the ammonium phosphate by means of the returning ammonium nitrate.

The corresponding equilibrium system has been studied in the NIUIF by A. I. Loginovaya and in the IONKh of the Academy of Sciences by Professor A. G. Bergman.

A mixture of ammonium phosphate and ammonium nitrate with any desired content of the latter may be obtained by a regular system of filtration.

Another method of improving the physical properties of the product and at the same time obtaining a triple fertilizer could be the fusion of a mixture of ammonium nitrate and ammonium phosphate with potassium chloride, which yields a nitrophoska fertilizer with any desired ratio between nitrogen, phosphorus, and potassium. This process has been studied by A. M. Dubovitskiy on the laboratory and pilot-plant scale in the NIUIF.

Numerous experiments have made possible the formulation of the production steps for the process (Cf Figure 2, page 108).

Flotation apatite is dissolved in 58 percent nitric acid. During the process of dissolution a 17-percent solution of sodium nitrate is introduced to precipitate the hydrofluosilicic acid in the form of Na_2SiF_6. The undissolved residue of the apatite mixed with the Na_2SiF_6 is separated from the solution by decantation, washed, and either turned out as a finished product -- insecticide -- or returned for further processing.

To precipitate out the rare earths the solution is neutralized by ammonia to a pH of 2 to 2.5. The precipitate of the phosphates of the rare earths -- the "concentrate" -- is separated by decantation from the solution.

The washed precipitate then goes for further processing to obtain fluorides of the rare earths.

A 40-percent solution of ammonium sulfate is mixed with the solution and CaO separated out as $CaSO_4 \cdot 2H_2O$. The calcium sulfate is separated by decantation from the solution and after washing goes into reaction with ammonium carbonate.

After separation of the calcium sulfate the solution is neutralized with ammonia and forms monoammonium phosphate. The return ammonium nitrate is then introduced into the hot suspension. The precipitated monoammonium phosphate is separated by decantation, filtered, and, without washing, mixed with potassium chloride and the mixture is ground.

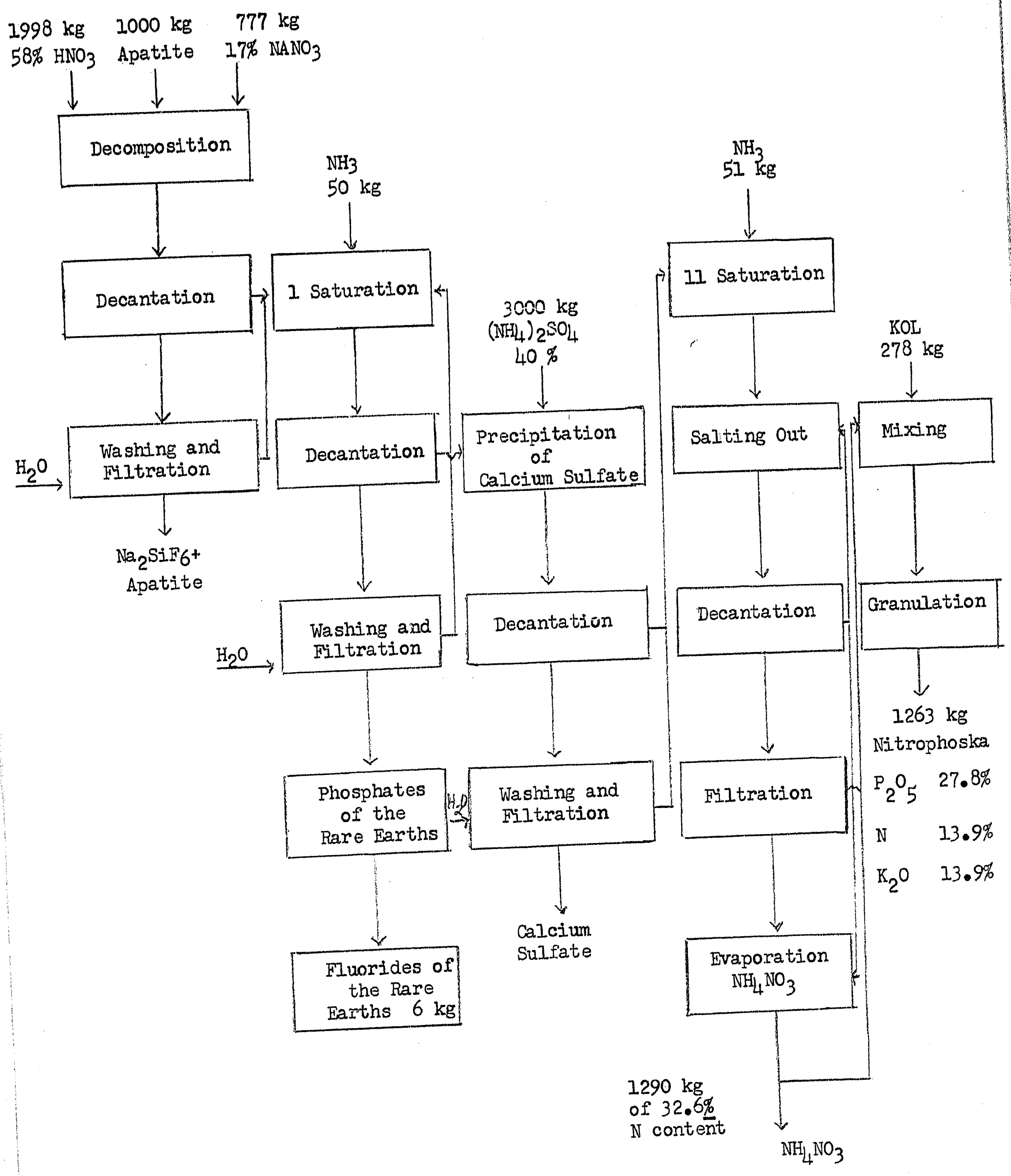

Figure 2. Lay-Out of Production Routing for "Azophoska" Production by Treatment of Apatite with Nitric Acid.

The solution of ammonium nitrate with 65 percent salts content is evaporated and part of it put out as a finished product while part of it is returned for use in salting out the ammonium phosphate.

The following are the coefficients of consumption in kilograms per 1,000 kilograms of apatite:

58-percent nitric acid	1,998
17-percent solution of $NaNO_3$	777
Ammonia gas	101
40-percent solution of ammonium sulfate	3,000
Potassium chloride	278

The yield in kilograms per 1,000 kilograms of apatite is as follows:

Insecticide containing about 42 percent Na_2SiF_6 (The quality of this product is subject to check on a pilot-plant scale.)	75
Rare earths concentrate (content 25 percent)	25
Azophoska, containing about 28 percent P_2O_5, 14 percent N and 14 percent of K_2O	126
Ammonium nitrate, containing about 32.6 percent N	1,290

At the present time laboratory studies on the above-described process with flotation apatite and Vyatka phosphorite have been completed. In 1937-1938 experiments with model apparatus involving the utilization of fluorine and the rare earths will be conducted. In spite of the interest of this method, we do not recommend immediate transition to industrial-scale production in view of the complexity of the process, which requires the elaboration of all details on a model or pilot-plant scale of equipment, as well as a number of technical and economic conditions.

IV

Thanks to the fact that in nitric acid dissolution of low-grade phosphorites containing large quantities of sequioxides the latter pass into solution to a relatively small extent, this method is of interest not only for flotation apatite but for most of our phosphorites as well. Even after roasting most of our low-grade phosphorites yield slimy slurries on dissolution by nitric acid -- slurries which are very hard to separate from the solution and to wash free of. For this reason the extraction and separation of the phases had to be done by way of decantation and counterflow rinsing to relatively weak dilutions of HNO_3 which would involve extremely great difficulties and increased expense in the subsequent evaporation of the $Ca(NO_3)_2$ solution, and might also cause loss of nitrogen. Future research on nitric acid dissolution of low-grade phosphorites, a considerable number of which have already been subjected to preliminary tests by the NIUIF and other research institutions, should be directed principally towards the elimination of these difficulties.

A number of technical and economic computations made by the NIUIF and GIPROAZOT showed that nitric acid dissolution of phosphorites was, on the average, not less than 10-15 percent cheaper, and for some types up to 30-40 percent cheaper, than sulfuric acid methods of making concentrated fertilizers.

In the future, besides the earliest-possible initiation of experiments with model or pilot-plant equipment for the preparation of dicalcium phosphate and calcium nitrate, it is also desirable to make a detailed study of A. P. Belopolskiy's suggestion for the preparation of $CaH_4P_2O_8$, a study of new variants for preparation of non-hygroscopic nitrosuperphosphate, and a number of technological details of the above-described production processes.

- END -