The invention relates to a complex nitrogen-phosphorus-potassium NPK-fertilizer, where mass fraction of total nitrogen is from 13-15%, mass fraction of total phosphates, in terms of $P_2O_5$, is from 9-10%, mass fraction of potassium, in terms of $K_2O$, is from 13-15%, and also to method for the preparation of said fertilizer from a solid phosphate salt, being a mixture of fluorapatite $Ca_3(PO_4)_2$ and dicalcium phosphate $CaHPO_4 \times nH_2O$, where $n$ is 0 to 2, with fluorapatite $Ca_3(PO_4)_2$ $F$ content from 27% to 99%, using various potassium and ammonium salts as a source of nutrients in the fertilizer. The technical result is providing enhanced properties of NPK-fertilizer, in particular a method for its production allows to improve the strength of granules, solve the problem related to the plasticity of granulated complex fertilizers, improve water solubility of phosphorus contained in the fertilizer by 98%, thereby improving consumer properties of NPK-fertilizers.

DESCRIPTION

The invention relates to the chemical industry and may be used in the field of complex mineral NPK-fertilizers production technology. NPK-fertilizer ("azophoska", "nitroammophoska") is a complex fertilizer possessing high economic efficiency and intended for use in growing different crops and in almost any soil. NPK type is characterized by mass fractions of nitrogen, phosphorus and potassium in a fertilizer.

Modern agrochemical science assumes the use of fertilizers with nutrients ratio N:P:K, namely N:P₂O₅:K₂O, in different ranges, which necessitates the development of technological methods providing the possibility to produce fertilizers with controlled nutrients ratio in accordance with consumer needs.

The present invention relates to preparation of granulated NPK-fertilizers from phosphate salt containing up to 99% fluorapatite, in particular said phosphate salt is a mixture of Ca₅(P₂O₅)₃F (fluorapatite), where n is 0 to 2, and Ca₅(P₂O₅)₃F content in phosphate salt is 27% to 99%, wherein the method allows to use various potassium and ammonium salts as sources of nutrients in the fertilizer.

The invention also relates to a continuous method for the preparation a granulated NPK-fertilizer from said phosphate salt consisting largely of fluorapatite. As potassium source, the
potassium salts are used, which are raw materials available on the market, in particular potassium sulfate $K_2S0_4$. As a nitrogen source, ammonium nitrate $NH_4NO_3$ is used.

PRIOR ART

RU 2216526 discloses a method for obtaining a NPK-fertilizer with adjustable $N:P_2O_5:K_2O$ ratio, said method comprising acid decomposition of phosphate raw material with nitric acid, adding nitrogen-containing component, neutralization with ammonia, mixing NP-slurry with potassium chloride or sulfate, granulation and drying of the target product.

Patents RU 2439039 and RU 2223933 also disclose the methods of phosphate rock decomposition with nitric acid accompanied by neutralizing slurry with ammonia and adding potassium salts.

Drawbacks of these methods are: the use of expensive and scarce component, i.e. nitric acid, as the acid, unsatisfactory consumer properties of granules due to their low strength and hydrochloric acid release during storage in case of using potassium chloride as a raw material. Product evaporation stage to attain residual moisture results in additional energy consumption, while the use of ammonia to neutralize the residual acid results in reduction of soluble phosphorus salts content in the product.

Patent RU 2107055 discloses method for the preparation of complex fertilizers by decomposition of phosphate rocks with a mixture of phosphoric and sulfuric acids with neutralization of the mixture with alkaline potassium salt such as potassium carbonate, followed by neutralization with ammonia. The drawback of this method is the use of extraction phosphoric acid, which is an expensive product, the production thereof is accompanied by generation of a large amount of waste, namely phosphogypsum, also a lot of water is introduced into the system together with phosphoric acid, which necessitates evaporation stage to obtain the final product. The use
of ammonia to neutralize the mixture reduces soluble phosphorus portion to less than 60%.

There are also some studies methods to carry out the method of producing complex fertilizers from soluble phosphate salts.

Chinese patent CN 1113900 (1994) discloses producing of a fertilizer containing nitrogen and phosphorus, wherein the fertilizer is produced from phosphate rock and nitric acid, and the resulting product is Ca(H$_2$P0$_4$)$_2$, which is crystallized; NH$_4$H$_2$P0$_4$ is obtained by mixing the ammonium nitrate with the mother liquor, and bubbling of the obtained mother liquor with ammonia yields CaHPO$_4$. The drawback of this method may include: the presence of evaporation stage in the method, in the product phosphorus is not in a water-soluble form of dicalcium phosphate, and the method of potassium introduction into fertilizer is not disclosed.

Patent GB 662079 discloses production of fertilizers containing soluble phosphorus salts based on the slurry resulting from decomposition of natural phosphates, DCP (dicalcium phosphate) or TCP (tricalcium phosphate). Phosphates are decomposed by sulfuric acid treatment, then the mixture is exposed to nitric acid to yield MAP and calcium nitrate. The product is stabilized by adding ammonium sulfate, whereby gypsum and ammonium nitrate are formed from calcium nitrate. Additional quantity of added ammonium sulphate has a favorable effect on the fertilizer, as double salt of ammonium sulfate with two ammonium nitrate molecules is formed. In the end ammonia gas is added to the mixture to achieve the formation of citrate-soluble phosphate – DCP from the residues of present MCP. The drawbacks include the presence of hygroscopic potassium nitrate in the system, which makes it difficult to method the mixture to obtain a granulated product, and the presence of dicalcium phosphate in the product, which reduces the water-soluble phosphorus forms content.
British patent GB 702 860 discloses the preparation of granulated NPK-fertilizers from raw material obtained from phosphate decomposition. In accordance with the description, MCP (monocalcium phosphate) is prepared by phosphate rock decomposition with nitric acid. The decomposition occurs in two steps. One of the drawbacks of granulated complex NP-fertilizers according to the description, is their plasticity. This problem was not solved in the production method.

Patent CN 1220236 (1997) discloses a method which comprises mixing of the hydrated lime with one or both substances: powdered \( \text{Ca}_3(\text{P}0_4)_2 \) and \( \text{CaHP}0_4 \), adding phosphoric acid with a concentration of 62% to 85% under stirring at 80°C for 20 to 60 seconds to give MCP (monocalcium phosphate), followed by curing for 8-100 hours, natural drying and grinding to yield the product. \( \text{H}3\text{P}0_4/\text{Ca}_3(\text{P}0_4)_2 \) or \( \text{H}_3\text{P}0_4/\text{CaHP}0_4 \) ratios are identical (7 to 16):100. The powdered \( \text{Ca}(\text{H}_2\text{P}0_4)_2 \) reacts with powdered \( \text{Ca(OH)}_2 \) to give \( \text{CaHP}0_4 \) and \( \text{Ca(OH)}_2/\text{Ca}(\text{H}_2\text{P}0_4)_2 \) ratio is (10 to 22):100. The drawbacks of this method include the use of hydrated lime, the production of which requires additional energy, the method is periodic (there is a product maturing stage).

Another methods for producing MCP are the methods of apatites decomposition with phosphoric acid. Apatite reaction with phosphoric acid:

\[
\text{Ca}_5(\text{P}0_4)_3\text{F} + 7\text{H}_3\text{P}0_4 \rightarrow 5\text{Ca}(\text{H}_2\text{P}0_4)_2 + \text{HF}
\]

The method, method and forms of the main products vary depending on which acids: \( \text{HCl}, \ \text{HNO}_3, \ \text{H}_2\text{SO}_4 \) and acid mixture are used as a starting material.

Chinese patent CN 1305946 discloses obtaining monocalcium phosphate (MCP) from phosphorite. This method includes reaction of phosphorite and sulfuric acid at temperatures ranging from 70°C to
95°C for 2-8 hours; filtration to obtain 10% to 30% phosphoric acid; adding CaCO₃ to phosphoric acid and removal of impurities; neutralization with Ca(OH)₂ and filtering; adding CaH₂PO₄ and CaO; and spray-drying to obtain Ca(H₂P₂O₇)₂ and a product with a high phosphorus content (core of calcium salts of phosphoric acid, 19-22% phosphorus). A disadvantage of this method is that one of the method stages is the production of an aqueous phosphoric acid solution, therefore, the need of water evaporation leads to additional costs associated with carrying out the method.

The authors of the patent MX NL03000044 (2003) consider conversions of monocalcium phosphate (MCP), calcium contained in the calcium superphosphates. 98% sulfuric acid, anhydrous ammonia, calcium oxide and MCP, DCP or TCP are used to obtain this product. During the first phase, monocalcium phosphate and phosphoric acid are obtained along with water from the starting superphosphate, and the solid insoluble components (calcium sulfate, calcium phosphate, iron phosphate and aluminum phosphate, fluorine compounds, unreacted starting phosphorus materials and other insoluble compounds such as silicon dioxide and silicates) are separated by decantation in water. The purified solution reacts with calcium hydroxide suspension to yield crystals suspension in DCP, which are then separated by decantation. The resulting crystals are then reacted with acid ammonium sulfate to give monoammonium phosphate solution, and insoluble crystals of calcium sulfate dihydrate are separated by filtration. In the last stage of reaction concentrated hydrochloric acid and ammonia are added to DCP suspension. Filtration yields a solution with MCP concentration of more than 48%. The drawbacks include: technological complexity of carrying out the method, the use of numerous reagents, product losses in precipitate during filtration and decantation, and also obtaining MCP in the form of a solution that complicates its further processing.
Mexican patent MX NL0500002 discloses method for the preparation of monocalcium phosphate MCP, sodium phosphate, potassium and MAP, where phosphate rock, sulfuric acid, calcium oxide, ammonium sulphate or potassium sulphate are used as starting materials. The important part is the method for producing phosphate salts, which are prepared by reacting DCP (dicalcium phosphate) with appropriate acid sulphates of the corresponding (magnesium, ammonium, potassium) salts. Upon gypsum filtration, the resulting MAP or other salts are concentrated in an evaporator and crystallized. The disadvantage of the method is the stage of salts solution preparation and gypsum filtration, which leads to additional costs associated with product solidification by evaporation. Using natural phosphate rock for decomposition results in a large quantities of waste — phosphogypsum.

In the industrial practice, MCP (monocalcium phosphate) is mainly prepared by reaction of calcium salts with phosphoric acid. An example is the reaction of $\text{H}_3\text{PO}_4$ with calcium containing compounds, such as lime milk, at a low temperature. Furthermore, it is possible to use reaction of finely ground limestone with phosphoric acid.

Another method includes preparation of calcium orthophosphate $\text{Ca}_3(\text{PO}_4)_2$, known as calcium phosphate, by treating a mixture of calcium sulphate and phosphoric acid with sulfuric acid or by reaction of sulfuric acid with calcium sulfate and monocalcium phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ mixture.

In fact, the NPK preparation is mainly carried out by decomposition of natural phosphates with acids. The state of the art comprises a method of preparation of a material which is simple superphosphate (SSP) or triple superphosphate (TSP), by reaction of phosphates with sulfuric or phosphoric acid. A soluble portion consists primarily of calcium monophosphate, and the insoluble part is a gypsum in case of SSP (and other insoluble impurities in addition to those contained in the gypsum).
During processing to obtain complex fertilizers, feedstock is granulated in drum granulators with the addition of a small amount of alkali (e.g. ammonia). Free phosphoric acid content, which is up to 5% in the powdered superphosphate, is reduced by 1-2% due to neutralization in the method of granulation. At the same time, a water soluble portion is reduced reaching the level of 60% in such methods.

The above prior art reveals the main aspects and disadvantages of reaction systems of complex fertilizers granulation.

The drawbacks of the known methods also comprise the fact that at the current stage of technology development the following issues associated with NPK complex fertilizers production remain problematic or unresolved:

- Complex fertilizers based on MCP (monocalcium phosphate) and ammonium nitrate are technologically problematic, caking problems are observed. The granulate obtained is flexible, which makes it difficult to manufacture using conventional granulation methods,

- During heating MCP may become dissolved in the "own" water.

Currently there are no known methods for industrial scale production of complex fertilizers, where phosphate part is included or present as monocalcium phosphate MCP, i.e. on the basis of superphosphate or triple superphosphate.

Thus, the present invention is aimed to develop a novel type of complex NPK-fertilizer having high water solubility of P₂O₅.

The problem is solved by producing NPK-fertilizer using K₂SO₄ as a potassium source and ammonium nitrate as a nitrogen source in the presence of MCP (monocalcium phosphate) and gypsum.

Since one of the requirements for the resulting fertilizer is high water solubility of P₂O₅, it is important to have all the product
obtained by decomposition of a complex phosphate salt substantially in the form of monocalcium phosphate MCP, or other phosphoric acid salt, which will provide water solubility. Also MCP should remain stable to prevent its conversion into dicalcium phosphate and phosphoric acid.

It should be noted that now sulfur is considered to be one of important nutrients in said type of fertilizers. According to the present invention the final product comprises anhydrous fine gypsum (calcium sulfate) providing access (for plants) to such element as sulfur, which is necessary and which is present in the target fertilizer introduced into the soil.

Thus, the present invention provides improvement of NPK-fertilizer properties, while a method for its production can improve the strength of granules, allows to solve the problem associated with plasticity of granulated complex fertilizers and thereby enhance consumer properties of NPK-fertilizers.

The solution of the problem results in high efficiency of the product obtained, reducing the cost of the final product and significant expansion of the raw materials base.

The present invention provides complex nitrogen-phosphorus-potassium fertilizer (NPK) comprising ammonium nitrate, anhydrous calcium sulfate, potassium dihydrogen phosphate, wherein the mass fraction of total nitrogen is from 13-15%, mass fraction of total phosphates, in terms of $\text{P}_2\text{O}_5$, is from 9-10%, mass fraction of potassium, in terms of $\text{K}_2\text{O}$, is from 13-15%.

The stated technical problem of obtaining such fertilizer is solved in that the method for the preparation of a complex NPK-fertilizer from a solid phosphate salt, being a mixture of fluorapatite and dicalcium phosphate, includes decomposing of said solid phosphate salt with sulfuric acid according to semi-dry method, adding
potassium sulfate as a potassium source, ammonium nitrate as a nitrogen source, preparing NPK slurry, and granulating and drying the final product.

This solid phosphate salt is a mixture of fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ and dicalcium phosphate $\text{CaHPO}_4 \times n\text{H}_2\text{O}$, where $n$ is 0 to 2, with fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$ content from 27% to 99%.

The technical result of practicing this method is that water soluble form of $\text{P}_2\text{O}_5$ reaches 98%. In other words, the phosphorus contained in the fertilizer is 98% water soluble. An important point of resolving the technical problem is the fact that practicing said technological method results in obtaining MCP (monocalcium phosphate) by reaction in the form of monohydrate (i.e., it remained stable). For this purpose, the temperature during dicalcium phosphate decomposition should not exceed 120°C. At this temperature dehydration begins.

An important aspect of the claimed method realization is adding potassium sulfate to MCP at one of the method stages, which provides substantially anhydrous gypsum in certain method conditions. Namely, reaction of MCP with potassium sulfate at the temperature not lower than 120°C provides substantially anhydrous gypsum.

Also, it should be emphasized that the conditions of the proposed method, namely that the temperature of the slurry obtained after preparing MCP and feeding to the reactor should not be less than 120°C, allow to avoid the formation of gypsum hemihydrate (which is highly undesirable for the resulting fertilizer).

Technological conditions for obtaining anhydrous gypsum in fine-dispersed form further ensure availability of essential fertilizer element, sulfur, upon fertilizer application in the soil.
In other words, the important aspect is that the method for producing involves the use of MCP in monohydrate form at the temperature not exceeding 120°C, which in turn avoids degradation of MCP to dicalcium phosphate and phosphoric acid.

**SUMMARY OF THE INVENTION**

The method of dicalcium phosphate (DCP) decomposition:

The contact of concentrated sulfuric acid and dicalcium phosphate results in forming MCP (monocalcium phosphate). The ingredients are mixed in equimolar ratio with respect to calcium in DCP (dicalcium phosphate) (equimolar amount of sulfuric acid is calculated according to DCP composition in chemical reactions (1) and (4)).

This method is chosen because DCP, as a starting material, is not a pure substance but rather a mixture, where, along with DCP, at least fluorapatite is present.

The methods taking place during mixing may be expressed by the following system of equations:

\[ H_2S0_4 + 2CaHP0_4 + H_2O \rightarrow Ca(H_2P0_4)_2 + CaS0_4 - 71.2 \text{ kJ/mol} \]  

(1)

More specifically, the reaction enthalpy refers to the following general equation:

\[ 2CaHP0_4 \cdot 2H_2O + H_2S0_4 = CaS0_4 + Ca(H_2P0_4)_2 \cdot H_2O + 3H_2O \]

In terms of mineralogy, DCP is commonly referred to as "brushite", which is dicalcium phosphate dihydrate. According to the results of RTG measurements of the provided sample DCP, it is present in an anhydrous form ("monetite"), therefore in equation (1) DCP is shown in anhydrous form. In accordance with RTG record after MCP preparation reaction, the resulting gypsum is in the form of anhydride and the reaction is exothermic.
As a result, the reaction 1 — MCP formation — proceeds in two stages:

\[ \text{H}_2\text{SO}_4 + \text{CaHP0}_4 \rightarrow \text{H}_3\text{P0}_4 + \text{CaSO}_4 \] (2)

\[ \text{H}_3\text{P0}_4 + \text{CaHP0}_4 \rightarrow \text{Ca(H}_2\text{P0}_4)_2 \] (3)

In parallel with the stage of phosphate salt decomposition, sulfuric acid reacts with fluorapatite.

\[ 7\text{H}_2\text{SO}_4 + 2\text{Ca}_5\text{P}(\text{PO}_4)_3 + 3\text{H}_2\text{O} \rightarrow 3\text{Ca(H}_2\text{P0}_4)_2\cdot\text{H}_2\text{O} + 7\text{CaSO}_4 + 2\text{HF} - 545.6 \text{ kJ/mol} \] (4)

This reaction is highly exothermic, unlike DCP conversion.

According to the mechanism, phosphates decomposition reaction occurs in two stages; in practice the second stage is slower and proceeds not quite up to the end:

\[ \text{Ca}_5\text{P}(\text{PO}_4)_3 + 5\text{H}_2\text{SO}_4 \rightarrow 3\text{H}_3\text{P0}_4 + 5\text{CaSO}_4 + 2\text{HF} \] (5)

\[ \text{Ca}_5\text{P}(\text{PO}_4)_3 + 7\text{H}_3\text{P0}_4 + 5\text{H}_2\text{O} \rightarrow 5\text{Ca(H}_2\text{P0}_4)_2\cdot\text{H}_2\text{O} + 2\text{HF} \] (6)

The resulting MCP is allowed to "degrade" in the presence of water to form DCP and phosphoric acid, from which, in turn, MCP is formed again as a result of the reverse reaction. This reverse reaction proceeds in the presence of water, so it is difficult to achieve high levels of water-soluble phosphorus (MCP) content in the reaction mixture. In practice, this is achieved by carrying out decomposition with low water content in the system.

\[ \text{Ca(H}_2\text{P0}_4)_2\cdot\text{H}_2\text{O} \leftarrow \Rightarrow \text{CaHP0}_4 + \text{H}_3\text{P0}_4 + \text{H}_2\text{O} \] (7)

It is necessary to obtain MCP in the form of monohydrate, because of this the temperature during DCP decomposition should not exceed 120°C as at this temperature the dehydration begins. In case of anhydrous MCP formation under lack of water or high temperature of the reaction mixture, hydration occurs in the method of slurry.
preparation with negative impact on the water balance and reaction medium viscosity and in conditions of hardly controllable accompanying temperature changes.

Production of NPK-fertilizer using potassium sulfate as a potassium source:

Reaction of MCP with potassium sulfate gives gypsum and potassium dihydrogen phosphate:

\[
\text{Ca}(\text{H}_2\text{P}_4\text{O})_2 + \text{K}_2\text{SO}_4 \rightarrow 2\text{KH}_2\text{PO}_4 + \text{CaSO}_4 \quad (8)
\]

The reaction proceeds in a saturated ammonium nitrate solution, which contains small amount of water at a high temperature. The system has molar excess of potassium sulphate; no free MCP remains in the system. The resulting gypsum is in anhydrous form at ambient temperature.

NPK product prepared using DCP, sulfuric acid, ammonium nitrate and potassium sulphate mainly comprises the following components:

- Ammonium nitrate
- Anhydrous calcium sulfate
- Potassium dihydrogen phosphate

The technological method for producing the claimed NPK-fertilizer according to the invention comprises the following steps:

1. Wet part - Slurry preparation
2. Dry part - Granulation
3. Recycling of waste gases and waste water

Wet part is a system of methods resulting in preparation of NPK slurry suitable for granulation:
phosphate salt (in particular the mixture of DCP and fluorapatite) decomposition with sulfuric acid to give monocalcium phosphate (MCP), the method is carried out in a fluidized bed mixer for optimum contact of the particles during the reaction. Conducting the reaction in a fluidized bed avoids dehydration of MCP monohydrate. After reaction in the mixer, ending of the reaction and waste gases release occurs in the maturing unit.

Further slurry preparation takes place in a cascade of three reactors equipped with stirrers.

When using potassium sulfate as a potassium source in the method of NPK preparation, a further scheme of the method is as follows:

- in the first reactor: MCP (monocalcium phosphate) reacts with ammonium nitrate to give ammonium monophosphate. Ammonium nitrate is dosed in the form of melt or granules through the dosing device;

- in the second reactor: potassium sulphate is fed through the dosing device, such potassium sulphate being fine enough for complete reaction to occur;

- the third reactor in the cascade is a maturing unit used prior to product granulation.

From the wet part of the method, slurry is fed to granulation step, which is carried out in the granulator of suitable design by agglomeration and layering in a fluidized bed. Returns are input to the front part of the granulator. Drying is carried out with hot air. After carrying out the following operations: screening, crushing, cooling, surface treatment with anti-caking additive, the finished product suitable for storage and transportation is obtained.

Waste gases containing dust of products and raw materials used in the production as well as gases released during production are
captured in wet scrubbers with the addition of neutralizing agents into absorbent.

Thus, the main object of the present invention is the production of NPK-fertilizer using K₂SO₄ as a potassium source and ammonium nitrate as a nitrogen source in the presence of MCP and gypsum. Due to strict requirements concerning P₂O₅ water solubility it is necessary to have essentially all the phosphorus feedstock in the form of MCP or other salt of phosphoric acid, which would provide water-solubility. MCP should remain stable in order to prevent its conversion to DCP and phosphoric acid.

Unlike other macronutrients, in case of phosphorus compounds to be applied into the soil, the main issue is their usefulness for plant nutrition. Accordingly, all fertilizers containing phosphorus are rarely evaluated for total phosphorus content. However, relative solubility criterion is always provided, such criterion is determined under certain conditions: in water (the most fast-acting form), in weak acids (2% citric acid or formic acid) or in solutions which can simulate soil conditions (for example, neutral or alkaline ammonium citrate solution).

Among calcium phosphates, only acid calcium phosphate, monocalcium phosphate (MCP), in the form of anhydrous salt Ca(H₂PO₄)₂ or monohydrate Ca(H₂PO₄)₂ × H₂O is water soluble. Middle calcium phosphate, dicalcium phosphate (DCP), is not water soluble and is found in the dihydrate form CaHPO₄ × 2H₂O or in the form of anhydrous salt CaHPO₄. Similarly, tricalcium phosphate Ca₃(PO₄)₂ is insoluble in water.

Thus, the whole proposed NPK production method can be divided into 2 main stages: the method of producing a water-soluble phosphate salt and the method of producing complex fertilizers from this salt.

According to the present invention, the production of complex NPK fertilizer consists of two main methods: wet (NPK slurry
production) and dry (granulation, milling, screening and cooling of the finished product) methods.

The following stage of the method will be described in more details:

1. Wet part

Fig. 1 is a diagram of wet method to give NPK slurry using potassium sulfate $K_2S0_4$ as a potassium source in the product.

The phosphate salt, being a mixture of calcium phosphates with fluorapatite (stream 1) together with sulfuric acid (stream 2) are fed into the flow device (unit A), which is a mixer with fast rotating blades and reaction mass maturing unit. Sulfuric acid is dosed in equimolar ratio to the phosphate salt. The method results in the following chemical reactions in the reaction mass in unit A:

$$H_2S0_4 + 2CaHP0_4 + H_2O = Ca(H_2P0_4)_2 + CaS0_4 \quad (1)$$

$$7H_2S0_4 + 2Ca_5(P0_4)_3F + 3H_2O = 3Ca(H_2P0_4)_2 \times H_2O + 7CaS0_4 + 2HF \quad (2)$$

In both cases the reactions take place in two stages: the reaction of phosphate with sulfuric acid and phosphoric acid release, the reaction of phosphoric acid with phosphate salt to give MCP (monocalcium phosphate). The reaction of MCP formation may occur not completely, in particular, due to MCP decomposition in the presence of water.

Reactions 1 and 2 are exothermic, especially the reaction 2. The technical solution for removing heat of reaction is a complex one: reactor is equipped with a water jacket and also part of the heat is removed from the system with exhaust gases and part of the heat is removed with water vapor. To ensure the removal of vapor and gases mixing unit A is operated under vacuum. Heat removal system
parameters must be adjusted so that the temperature of the reaction mixture does not exceed 120°C.

After mixer the reaction mixture is fed into maturing unit, being a part of unit A, which is a device with a stirrer. The following methods take place in the maturing unit:

- completion of the reaction methods;
- final removal of gases from the reaction mixture;
- averaging of the chemical and physical properties of the reaction mass.

Further slurry preparation is carried out in a cascade of three reactors (units B, C, D) with a stirrer and a heating jacket equipped with an overflow.

The first slurry reactor (unit B):

The main agent of the method in the reactor is ammonium nitrate. It is supplied in granulated form. Two approaches can be used to input it into the system:

1. Prior to inputting to the system ammonium nitrate is melted in a separate reactor to give melt, then aqueous solution containing 93-97% ammonium nitrate at about 158°C is dosed into the first slurry reactor.

2. Ammonium nitrate is input into the system in the form of granules, which are dosed into the first slurry reactor using a dosing device.

Ammonium nitrate in the form of granules or melt (stream 5) is fed to reactor unit B, depending on the product composition MCP monohydrate (along with formed gypsum) is fed and water in the form of vapor (stream 4) is added in the needed quantity. The reactor mixture is maintained at a temperature not exceeding 160°C. The heat
is transferred by steam jacket and direct steam. No chemical methods take place in the reactor, the mixing gives homogeneous slurry in the saturated ammonium nitrate solution. MCP is partly dissolved and some part remains insoluble, gypsum remains anhydrous, it does not dissolve in the system.

The second slurry reactor:

Slurry from the first reactor (stream 6) is supplied via an overflow to the reactor (unit C), potassium sulfate (stream 7) is dosed using a dosing device. Reaction of MCP with potassium sulfate gives gypsum and potassium dihydrogen phosphate:

\[ \text{Ca(H}_2\text{P}_2\text{O}_7)^2 + \text{K}_2\text{SO}_4 = 2\text{KH}_2\text{PO}_4 + \text{CaSO}_4 \] (4)

To achieve completion of the reaction, disappearance of MCP, forming the substitution reaction products and obtaining a low viscosity mixture it is necessary to carry out the method at a temperature preventing gypsum hemihydrate formation, i.e. minimum 120°C, and feed sulphate with sufficiently small particle size.

The third slurry reactor:

Slurry from the second reactor (stream 8) is fed via the overflow to the third reactor (unit D). This reactor acts as a compensator for this product prior to granulation. The temperature is maintained in the range of 125°C to 145°C. After the third reactor slurry enters the dry method (stream 9).

Hydrogen fluoride is captured in unit F.

The stream of vapor and low pressure gases from the mixer (stream 3) is fed to the absorption column, where hydrogen fluoride is captured using the main solution (slurry of calcium carbonate or calcium hydroxide, alkali metals hydroxides solutions). The end product, metal fluorides, is washed and, according to the
application, is either recycled or dried and packaged and then sent to a warehouse.

Such NPK product prepared using phosphate salt, sulfuric acid, ammonium nitrate and potassium sulphate mainly comprises the following components:

- Ammonium nitrate
- Anhydrous calcium sulfate
- Potassium dihydrogen phosphate

The range of nutrients ratios in the produced type of NPK-fertilizer is illustrated in the following examples.

2. Dry part

Slurry at the temperature 125°C to 145°C flows by gravity from the third reactor to the granulator of paddle mixer type. Returns are input to its front part. Distributor distributes slurry in the material within the granulator. Granulation is carried out by agglomeration and layering in a fluidized bed, which is created by blades mounted on two shafts. Steam with pressure 0.3 to 0.4 MPa may be fed to granulator to adjust the optimal operating conditions of the granulator (temperature, humidity) according to the quality of the combined fertilizer produced. Wet granules at a temperature in the range of 90°C to 110°C, depending on the composition of the fertilizer, with water content of 1.5-3 wt% fall to the drying drum from granulator tray via a chute. The last chemical reactions may occur during granulation and drying.
Examples

Example 1

The basic method used is described above with reference to the scheme in Fig. 1.

The resulting complex nitrogen-phosphorus-potassium fertilizer (NPK) contains ammonium nitrate, anhydrous calcium sulfate, potassium dihydrogen phosphate, wherein mass fraction of total nitrogen is from 13-15%, mass fraction of total phosphates, in terms of P2O5, is from 9-10%, mass fraction of potassium, in terms of K2O, is from 13-15%.

Technological conditions of the method realization allow to obtain complex NPK-fertilizer of 15:10:15 type, which corresponds to mass fraction of total nitrogen, mass fraction of total phosphates, in terms of P2O5, and mass fraction of potassium, in terms of K2O.

According to one embodiment of the invention, the production of the above NPK based on solid phosphate salt, being a mixture of fluorapatite Ca5(PO4)3F and dicalcium phosphate CaHPO4·nH2O, where n is 0 to 2, with fluorapatite Ca5(PO4)3F content from 27% to 99%, allows the use of potassium sulfate and ammonium nitrate.

As raw material phosphate salt is used, said salt is obtained by decomposition of phosphoric rock with hydrochloric acid, separating the insoluble precipitate, followed by precipitation of solid phosphate salt using calcium carbonate slurry. For the production of the phosphate salt the rock from Keysik deposits was used.
The method gives a mixture of fluorapatite $\text{Ca}_5\left(\text{PO}_4\right)_3\text{F}$ and dicalcium phosphate $\text{CaHPO}_4 \times n\text{H}_2\text{O}$, where $n$ is 0 to 2, which is used in further production method of NPK composition:

Fluorine contained in the phosphate salt and obtained by decomposition of phosphate rock with hydrochloric acid is present in the mixture in the form of fluorapatite, which is confirmed by
analytical control of the samples. Phosphate salt containing 27% fluorapatite is further used for NPK production, namely:

The stage of decomposition of said solid phosphate salt with sulfuric acid is carried out at the temperature 115°C using semi-dry method, where decomposition takes place with low water content. This necessary condition is due to the selection of equimolar ratios in the system to maintain stability of MCP in monohydrate form. More specifically, to a phosphate salt [100 kg/h] in the mixer with fluidized bed 98% sulfuric acid [38 kg/h] is fed in the equimolar ratio. The method is conducted under vacuum for better removal of released gases, mainly hydrogen fluoride. The reaction mass is fed through maturing unit into the cascade of reactors with stirrer. Gas, mainly hydrogen fluoride, is supplied to the absorption step. The method is carried out at a temperature not exceeding 120°C.

Further, to the first reactor in the cascade of reactors ammonium nitrate [106 kg/h] is fed, the method is carried out at 125°C, potassium sulfate [161 kg/h] is fed into the second reactor. Upon completion of the method in the third reactor, the mixture is fed into the dry part of the method; granulation and drying result in production of a complex NPK fertilizer with component composition

$$\text{N:P}_2\text{O}_5\text{K}_2\text{O} = 15:10:15$$

containing sulfur in the form of fine-dispersed anhydrous gypsum.

**Example 2**

The basic method used is described above with reference to the scheme in Fig. 1.

The resulting complex nitrogen-phosphorus-potassium fertilizer (NPK) contains ammonium nitrate, anhydrous calcium sulfate, potassium dihydrogen phosphate, wherein mass fraction of total nitrogen is from 13-15%, mass fraction of total phosphates, in terms
of $P_2O_5$, is from 9-10%, mass fraction of potassium, in terms of $K_2O$, is from 13-15%.

According to one embodiment of the invention, the production of the above NPK based on solid phosphate salt, being a mixture of fluorapatite $Ca_5(P0_4)_3F$ and dicalcium phosphate $CaHPO_4 \times nH_2O$, where $n$ is 0 to 2, with fluorapatite $Ca_5(P0_4)_3F$ content from 27% to 99%, allows the use of potassium sulfate and ammonium nitrate.

As raw material phosphate salt is used, said salt is obtained by decomposition of phosphoric rock with hydrochloric acids similar to Example 1.

The method gives a mixture of fluorapatite$Ca_5(P0_4)_3F$ and dicalcium phosphate $CaHPO_4 \times nH_2O$, where $n$ is 0 to 2, which is used in further production method of NPK composition:

<table>
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<tr>
<th>Substance</th>
<th>Unit</th>
<th>Content</th>
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</thead>
<tbody>
<tr>
<td>$P_2O_5$, total</td>
<td>%</td>
<td>41</td>
</tr>
<tr>
<td>Cl</td>
<td>%</td>
<td>0.2</td>
</tr>
<tr>
<td>F</td>
<td>%</td>
<td>3.73</td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
<td>37</td>
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</table>

Fluorine contained in the phosphate salt and obtained by decomposition of phosphate rock with hydrochloric acid is present in the mixture in the form of fluorapatite, which is confirmed by analytical control of the samples. Phosphate salt containing 99% fluorapatite is further used for NPK production, namely:

The stage of decomposition of said solid phosphate salt with sulfuric acid is carried out at the temperature 115°C using semi-dry method, where decomposition takes place with low water content.
This necessary condition is due to the selection of equimolar ratios in the system to maintain stability of MCP in monohydrate form. More specifically, to a phosphate salt [100 kg/h] in the mixer with fluidized bed 98% sulfuric acid [38 kg/h] is fed in the equimolar ratio. The method is conducted under vacuum for better removal of released gases, mainly hydrogen fluoride. The reaction mass is fed through maturing unit into the cascade of reactors with stirrer. Gas, mainly hydrogen fluoride, is supplied to the absorption step. The method is carried out at a temperature not exceeding 120°C.

Further, to the first reactor in the cascade of reactors ammonium nitrate [106 kg/h] is fed, the method is carried out at 125°C, potassium sulfate [161 kg/h] is fed into the second reactor. Upon completion of the method in the third reactor, the mixture is fed into the dry part of the method; granulation and drying result in production of a complex NPK fertilizer with component composition N:P₂O₅:K₂O = 13:9:13 and also 13:10:13 containing sulfur in the form of fine-dispersed anhydrous gypsum.

**Example 3**

The basic method used is described above with reference to the scheme in Fig. 1.

According to one embodiment of the invention, the production of the above NPK based on solid phosphate salt, being a mixture of fluorapatite Ca₅(PO₄)₃F and dicalcium phosphate CaHPO₄ x nH₂O, where n is 0 to 2, with fluorapatite Ca₅(PO₄)₃F content from 27% to 99%, allows the use of potassium sulfate and ammonium nitrate.

As raw material phosphate salt is used, said salt is obtained by decomposition of phosphoric rock with hydrochloric acids similar to Examples 1 and 2.
The resulting complex nitrogen-phosphorus-potassium fertilizer (NPK) contains ammonium nitrate, anhydrous calcium sulfate, potassium dihydrogen phosphate, wherein mass fraction of total nitrogen is 14%, mass fraction of total phosphates, in terms of P$_2$O$_5$, is from 9-10%, mass fraction of potassium, in terms of K$_2$O, is from 14%.
CLAIMS

1. A complex nitrogen-phosphorus-potassium fertilizer (NPK), characterized in that it contains ammonium nitrate, anhydrous calcium sulfate, potassium dihydrogen phosphate, wherein mass fraction of total nitrogen is from 13-15%, mass fraction of total phosphates, in terms of P₂O₅, is from 9-10%, mass fraction of potassium, in terms of K₂O, is from 13-15%.

2. A method for the preparation of a complex NPK fertilizer of claim 1 from solid phosphate salt, being a mixture of fluorapatite Ca₅(PO₄)₃F and dicalcium phosphate CaH₂PO₄·nH₂O, where n is 0 to 2, with fluorapatite Ca₅(PO₄)₃F content from 27% to 99%, comprising the following stages:

   - the stage of decomposition of said solid phosphate salt with sulfuric acid using semi-dry method,

   - the stages of adding potassium sulfate as a potassium source, ammonium nitrate as a nitrogen source,

   - the stage of preparing NPK slurry, and also the stage of granulation and drying of the final product.

3. A method of claim 2, wherein the method is continuous.

4. A method of claim 2, wherein hydrogen fluoride resulting from said solid phosphate salt decomposition is captured.

5. A method of claim 2, wherein decomposition of said solid phosphate salt is carried out with sulfuric acid concentration of 96-98%.

6. A method of claim 2, wherein the sulfuric acid and said solid phosphate salt are fed to the reaction mass in the equimolar ratio.
7. A method of claim 2, characterized in that the semi-dry method is a decomposition of the phosphate salt with sulfuric acid under low water content conditions in the system.

8. A method of claim 2, wherein decomposition of said solid phosphate salt with sulfuric acid is carried out at the temperature 110°C to 120°C.

9. A method of claim 7, wherein the product of decomposition of said solid phosphate salt is calcium monophosphate (CaP), which is present in a monohydrate form.

10. A method of claim 2, wherein decomposition of said solid phosphate salt with sulfuric acid is carried out in a fluidized bed.

11. A method of claim 2, wherein decomposition of said solid phosphate salt with sulfuric acid is carried out under vacuum with possible removal of hydrogen fluoride to the absorption system.

12. A method of claim 2, wherein gypsum (CaSO₄) formed as a result of decomposition of said solid phosphate salt, in particular its fluorapatite part, is present in the reaction mass and in the final product mainly in the anhydrous form.
Fig. 1
INTERNATIONAL SEARCH REPORT

According to International Patent Classification (IPC) and/or both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C05B  C05C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
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<td>wo 2014/045301 A2 (INDO GULF FERTILIZERS [IN]) 27 March 2014 (2014-03-27) page 11, line 8 - line 20; examples 1,3</td>
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<tr>
<td>Y</td>
<td>GB 1 183 938 A (FISONS LTD) 11 March 1970 (1970-03-11) page 1, line 27 - line 63</td>
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:
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- P: document published prior to the international filing date but later than the priority date claimed

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"S" document member of the same patent family

Date of the actual completion of the international search: 15 August 2017

Date of mailing of the international search report: 22/08/2017

Name and mailing address of the ISA/
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer
Cardin, Aurelie
<table>
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