NPK-fertilizers produced by joint ammoniation of nitric and phosphoric acids mixture

Viacheslav Kolpakov

Relevance of work

The development of new and modernization of existing mineral fertilizers technologies is an integral part of the sustainable progress of the industry. It is especially important to resolve this issue in regard to introduction of the best available technologies in the Russian Federation. The development and implementation of new innovative process solutions are based on knowledge of the physical and chemical basis of the processes, the properties of semiproducts and final products formed by them, and, eventually, the consumer properties of granular mineral fertilizers. New products should have certain advantages over existing ones in the market.

Purposes and tasks of the work

The aim of the work is to develop new scientifically proved process solutions for production of concentrated nitrate-containing NPK-fertilizers for newly constructed and modernized existing process systems.

To achieve this goal, and taking into account the information from literature, the following tasks were solved:

- the chemical and phase composition of the system formed by joint neutralization of nitric and wet phosphoric acids mixture with ammonia as the basis for the fertilizers production such as nitrodiammophoska was studied;

- the impact of phase and chemical fertilizers composition on their physical, chemical, structural and mechanical properties was studied;

- the thermal stability of semiproducts and final products formed in the process of production of complex nitrate-containing fertilizers was studied;

- the rheological properties of reference slurries of various compositions specific for reaction slurries in the NPK-fertilizers production process were studied;

- the process and equipment solutions for implementation of the production process of a number of nitrate-containing NPK-fertilizers, ensuring the technology and products safety, as well as improving their consumer properties, were developed.

Scientific novelty of the work

1. The chemical and phase compositions of nitrate-containing NPK- and NP-fertilizers obtained at various degrees of neutralization have been determined. The main crystalline phases are: NH_4Cl, the content of which practically does not change with an increase in the degree of neutralization, $(NH_4)_2HPO_4$, the proportion of which is continuously increasing, and various double salts and solid solutions: $(K_{0,952}(NH4)_{0,048})NO_3$, $K_{0,37}(NH_4)_{0,63})H_2PO_4$, $2KNO_3 \cdot (NH_4)_2SO_4$, $(K_{0,70}(NH_4)_{0,30})_2SO_4$, the total content of which decreases with an increase of the neutralization degree, which is due to a decrease in the content of NH_4NO_3 and $NH_4H_2PO_4$, which enter into conversion interactions with KCl and $(NH_4)_2SO_4$.

2. The rheological characteristics (viscosity, density) of the reaction slurries have been established using rotational viscometry for the stages: neutralization of acids mixture with ammonia; introduction of ammonium sulfate and potassium chloride. For the dependences of the viscosity on moisture content, temperature and the compositions of the obtained NPK-fertilizers, the empirical equations describing them are proposed in the form $\eta = f(T, W)$, where η - viscosity; T - temperature; W - moisture,% mass. In this case, the discrepancy between the calculated and experimental data does not exceed 10%.

3. It was found that with an increase in the neutralization rate, expressed by the molar ratio NH_3:H_3PO_4 from 1,0 to 1,9 mol/mol, the amount of the heat release and the weight loss of nitrate-containing NPK-fertilizers samples decrease by approximately 1,7 times, that is explained by increase of the content of diammonium phosphate and ammonium sulfate, which are inhibitors for the thermal decomposition of nitrate components. The products with high total nitrogen content and low neutralization rate (grade 22:11:11) are thermally less stable than just ammonium nitrate due to their high content of nitrate nitrogen and the catalytic effect of chlorides on the thermal decomposition.

4. For the first time, there were established quantitative indicators for the effect of neutralization rate on the composition and the main physical and mechanical properties of granular NPK-fertilizers: an increase in molar ratio from 1,0 to 1,6÷1,7 mol/mol for various brands helps to reduce the caking tendency by 10÷60 % and the hygroscopic coefficient by 3÷40%.

Practical significance of the work

1. A new flexible technology for the production of various grades of nitrate-containing NPK-fertilizers with use of the existent equipment operating in the industry were proposed.

2. A fire- and explosion-proof, energy-saving and environmentally friendly method for production of nitrate-containing NPK-fertilizers with increased thermal stability were proposed and tested in industrial conditions. Patent for invention No. RU2541641C1 "Method of production of complex fertiliser" was received.

3. The optimal conditions (molar ratio, temperature, slurry moisture) for carrying out the stages of acids mixture neutralization and introduction of powdery raw materials into the slurry, granulation and granules drying were determined.

4. The initial data for the design of a new production facility of granular nitrate-containing NPK-fertilizers with a capacity of 900 000 TPA were developed and issued. In 2019, an apparatus of pre-neutralizer and a new two-stage neutralization scheme were introduced at the process system No. 3, section No. 2 of the Mineral Fertilizer Production Plant of JSC “Apatit”.

5. The developed and implemented process solutions were included in the advanced technologies section of the information and technical reference book on the best available technologies No. 2-2019 as well as in the list of state-of-the art technologies for investment contracts No. 3143-p, approved by the Government order of the Russian Federation dated November 28, 2020.

Statements to be proved during thesis defense

1. Impact of chemical and phase composition on consumer characteristics of the products.

2. Determination of the rheological characteristics of reference slurries for separate stages of nitrate-containing NPK-fertilizers production.

3. Study of the effect of the magnesium-containing additive on the physical and mechanical properties of fertilizers.

4. Research on explosion and fire hazard of the process and the products.

5. Process solutions for organizing a new process for nitrate-containing NPK-fertilizers production.