# TECHNOLOGY OF NITRIC ACID PROCESSING OF WASTE ENRICHMENT OF PHOSPHORITES OF CENTRAL KYZYLKUM

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***Abstract***. *Information is provided on nitric acid processing of phosphorite enrichment waste from the Central Kyzylkum region into liquid nitrogen-calcium fertilizers and fertilizer precipitate in one technological cycle and optimal technological parameters for processing liquid nitrogen-calcium fertilizers into granular calcium nitrate.*
***Keywords:*** *phosphorite enrichment waste, nitric acid, liquid fertilizers, precipitate, granulated calcium nitrate, technological scheme.*

## INTRODUCTION

More than half of the irrigated lands of Uzbekistan are subject to salinization, as a result of which their productivity is 1.5-2.5 times lower than that of non-saline soils [1]. Salinity also worsens the technological qualities of raw cotton. The most effective way to increase the salt tolerance of crops is the use of calcium nitrate [2].

Calcium occupies a special place in maintaining the balance of elements in plant tissues during salinity. With an increase in the concentration of aluminum, magnesium, sodium, chlorine and other elements in cotton tissues, calcium deficiency worsens [3]. The need for calcium for higher plants is so pronounced that it often manifests itself at the germination stage. Seedlings begin to suffer before seed reserves are exhausted, which is due to the soaking of seeds in calcium nitrate solutions, which also helps to increase seed germination.

It has also been established that the provision of cotton with calcium significantly reduces the toxic effect of salinity ions on growth, development and productivity. Considering that the area of saline lands exceeds 60% and the need of the agrochemical complex of Uzbekistan for calcium nitrate is more than 300 thousand tons per year, and its production is absent in the republic, this makes the problem of producing calcium nitrate one of the most pressing.

Calcium nitrate is a by-product of the production of complex nitrogen-phosphorus fertilizers obtained by nitric acid decomposition of phosphorus-rich apatite raw materials. Due to the presence of four water molecules in its composition, calcium nitrate has poor physicochemical properties. Many works have been devoted to improving the physicochemical and mechanical properties of calcium nitrate tetrahydrate [4-6].But none of the developed methods have found industrial application. In industrial conditions, liquid nitrogen-calcium fertilizers (LNCF) based on calcium-containing water treatment waste are produced in small volumes, due to the limited amount of calcium-containing waste in the spring-summer period [7].

## METHODS

To increase the volume of production of LNCF and reduce the cost of nitrogen in the fertilizer, calcium-containing waste from the enrichment of phosphorites of the Central Kyzylkum (CK) with mineralized mass (MM) is used as a calcium-containing source. The MM mass has the composition (wt. %): $P_2O_5$-12,86; CaO – 42,80; MgO – 0,80; $Fe_2O_3$ – 1,37; $Al_2O_3$- 1,17; $CO_2$ – 12,81; $SO_3$ – 2,00; F- 1,85 with calcium module 3.17, n.o. – 11.89 and are particles smaller than 7 mm. To conduct research on the decomposition of MM of nitric acid, a mineral fraction of up to -1 mm is used. Chemical analysis of initial, intermediate and final products using known methods [8-10].

**RESULTS AND DISCUSSION**

At the first stage, the MM was decarbonized with 57% nitric acid based on 100% $CO_2$ content. MM treatment was carried out in a setup simulating a prereactor. The MM was quickly treated in the cylindrical part of the prereactor with nitric acid and washed with water through the conical part into the decomposition reactor. The amount of water was calculated for the formation of a 40% nitric acid solution for decomposition at a total rate of 57% acid and 105% for complete decomposition of MM. The remainder of the nitric acid was simultaneously introduced into the reactor and kept under stirring for 30 minutes. After a given time, the nitric acid slurry was transferred to a reactor for ammoniation with ammonia gas.

Technological parameters for the decomposition of MM with nitric acid were selected from previously established studies on the decomposition of phosphorites with nitric acid [11-13]. A nitric acid concentration of 40% was chosen to obtain pulp in a decomposition reactor with a density of 1.55-1.56 t/$m^3$. This helps reduce foaming and intensify the process of producing nitric acid pulp.

As a result of ammoniation of nitric acid pulp to pH 6.5-7 and subsequent filtration, two types of fertilizers were obtained - liquid nitrogen-calcium (LNCF) and phosphorus-containing fertilizer precipitate (FP) in one technological cycle. The principal technological flow diagram for processing MM to obtain LNCF and FP is shown in Figure 1.

The table shows that with increasing pH, the content of all forms of $P_2O_5$ and CaO increases. FP at pH 7.2 contains 21.29% $P_2O_{5gen.}$., 15.56% $P_2O_{5ass.}$, 34.26% $CaO_{gen.}$ and 31.42% $CaO_{ass.}$.Table 1 shows the composition of the solid phase after ammoniation of acidic pulp depending on pH. The table shows that with increasing pH.

***Table 1***

***Chemical composition of the solid phase***

| № | pH | Chemical composition, mass. % | | | | $P_2O_{5ass.}$ / $P_2O_{5gen.}$ % | $CaO_{ass.}$ / $CaO_{gen.}$ % |
|---|---|---|---|---|---|---|---|
| | | $P_2O_{5gen.}$ | $CaO_{gen.}$ | $P_2O_{5ass.}$ | $CaO_{ass.}$ | | |
| 1 | 3 | 19,95 | 32,12 | 14,13 | 23,88 | 70,83 | 74,34 |
| 2 | 5,2 | 20,23 | 33,65 | 14,71 | 30,21 | 72,71 | 89,78 |
| 3 | 7,2 | 21,29 | 34,26 | 15,56 | 31,42 | 73,08 | 91,71 |

The liquid phase is represented by calcium and ammonium nitrates and contains 8% nitrogen and 49.4% calcium nitrate.

LNCF, with all its advantages over granular fertilizers, are seasonal, which limits their release in the autumn-winter period. To eliminate this drawback, research has been carried out on the production of granular fertilizers based on LNCF. The production of granular nitrogen-calcium fertilizer based on LNCF will not only increase the production of cheap nitrogen fertilizers for saline and slightly saline soils, but also process phosphorite enrichment waste year-round, the amount of which exceeds 14 million tons [14].

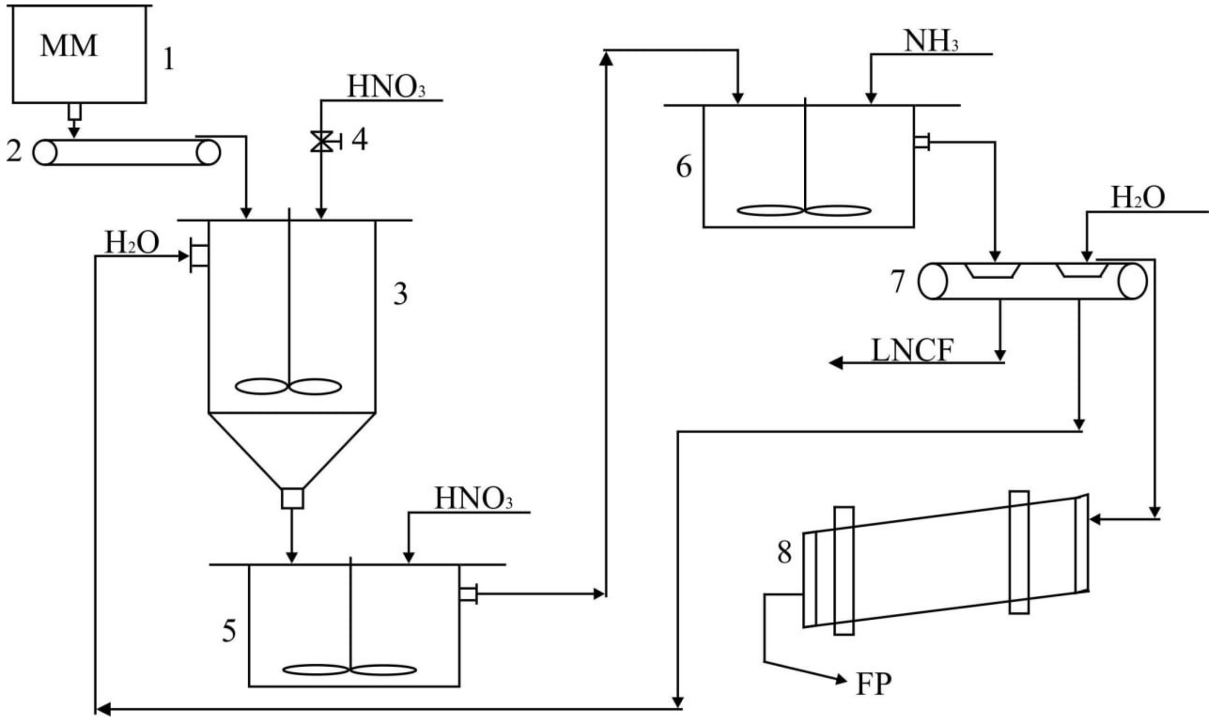


***Figure 1. Basic technological scheme for processing MM with the production of LNCF and fertilizer precipitate***

Research on the production of granular calcium nitrate was carried out in a pilot plant, consisting of a reactor with heating, a pump and a drum-granulator-dryer (DGD) apparatus with a diameter of 0.8 m, a length of 3 m, an inclination angle of 3 ° C and a productivity of 50 kg of product per hour. As a calcium nitrate solution, we used LNCF, obtained by decomposing MM with 40% nitric acid at a rate of 105% of stoichiometry, ammoniated to pH 7 and with a density of 1.55 – 1.65 g/cm$^3$.

The LNCF solution was evaporated in a heated reactor to a moisture content of 15-20%, 5-7% MM by weight of the melt was introduced, mixed and pumped to the pneumatic nozzles of the BGS apparatus. A fine fraction of nitroammophos was used as a cushion.

The optimal technological parameters for the operation of the BGS apparatus have been established: the temperature of the flue gases at the inlet is 350-400 °C, at the outlet 110-115 °C, the temperature in the product layer is 105-110 °C.

At temperatures below 350°C, the product contains moisture and clumps into huge lumps and sticks to the walls of the BGS.

When the flue gas temperature at the inlet is 350-400°C, the process proceeds normally, without any difficulties, with a good curtain. As a result, granules measuring 2-4 mm are formed, the proportion of which exceeds 95%. The share of small (less than 2 mm) fraction does not exceed 4%.

The resulting granular commercial product is characterized by the following quality indicators: mass fraction of calcium nitrate in terms of CaO 32-33.3%, mass fraction of total nitrogen 14-15%, mass fraction of ammonia nitrogen 0.9-1.05%, mass fraction of water 0 .4-0.6%, mass fraction of insoluble residue no more than 0.5%, granule strength 8-9 mPa, friability 100%, bulk weight without compaction 1.08 t/m$^3$, with compaction 1.15 t/m$^3$. The resulting granular calcium nitrate does not cake and retains 100% flowability after 1 year of storage.

**CONCLUSIONS**

Thus, the research carried out made it possible to find a technical solution that allows separating nitric acid pulp based on MM - waste from the enrichment of phosphorites of the Central Kyzylkum, to obtain two types of fertilizers in the form of LNCF and FP, to establish the possibility of granulating LNCF in BGS devices to obtain calcium nitrate with improved physicochemical and mechanical properties.

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