

DEVELOPMENT OF TECHNOLOGY FOR PROCESSING WASTE ENRICHMENT OF PHOSPHORITES OF THE CENTRAL KYZYL KUM FOR PHOSPHORUS AND NITROGEN-CALCIUM FERTILIZERS

¹Haydarov Bekzod, ²Shukurov Abduvali, ³Yusufova Nazokat

^{1,2}Tashkent Institute of Chemical Technology, Yangiyer branch, assistant teacher

³Student of the Yangiyer branch of the Tashkent Institute of Chemical Technology

<https://doi.org/10.5281/zenodo.10654878>

Abstract. *The world's population has exceeded 8 billion people and the problem of food supply has become even more acute due to the reduction of arable land, fresh water reserves and soil salinization. Mineral fertilizers are the main factor ensuring the growth of agriculture. The chemical industry of the Republic meets the needs of the agro-industrial complex with nitrogen and potassium fertilizers in sufficient quantities, which cannot be said about phosphorus-containing fertilizers. Of all the types of mineral fertilizers produced in the country, only simple, enriched superphosphates and nitrocalcium phosphate fertilizers contain calcium, which is a macronutrient and helps reduce soil salinity. All this indicates the need to increase the production of phosphorus- and calcium-containing fertilizers.*

Keywords: *nitrocalcium, ammoniation, nitric acid decomposition, mineralized mass.*

Throughout the world, the production of phosphate fertilizers is based on the use of rich phosphate raw materials. Intensive exploitation of rich deposits leads to their depletion. Therefore, all over the world there is a search for ways to involve poorer, more accessible raw materials, such as the phosphorites of the Central Kyzylykum, in the production of phosphate fertilizers.

Phosphorites of the Central Kyzylykum are characterized by a low phosphorus content (16.2% P₂O₅) and a high calcium module (2.85-3.50). In addition, when enriching such raw materials, enrichment waste is formed - mineralized mass (MM), etc., which is not processed and stored. The Kyzylykum phosphorite plant has accumulated more than 14 million tons of MM with an average content of 13.75% P₂O₅. This amounts to approximately 1.56-1.82 thousand tons of P₂O₅. Nitric acid decomposition of unenriched phosphate raw materials (NPR) and MM is the most economical method of their processing compared to other acids. To involve NFS and MM in industrial production, it is necessary to justify a number of scientific decisions, including in the following areas: the development of an effective method for separating the liquid and solid phases of decomposition products of NFS and MM with nitric acid, the influence of the degree of ammoniation on the behavior of the components of the nitric acid extract, the development of a cost-effective, waste-free technology for processing NFS and MM, development of technology for processing the liquid and solid phases of decomposition products of NFS and MM into various types of liquid and solid fertilizers.

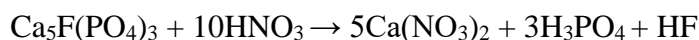
In the Republic, as a result of the implementation of specific large-scale measures, high results have been achieved in scientific research on the development of technology for processing phosphorites of the Central Kyzylykum and providing the agro-industrial complex with phosphorus-containing fertilizers. In the third direction of the new development strategy of Uzbekistan for 2022-2026, the important tasks are defined as "...continuing the implementation of

industrial policy aimed at ensuring the stability of the national economy, increasing the share of industry in the gross domestic product and increasing the volume of industrial production by 1.4 times ... ". In this aspect, the development of a rational, cost-effective technology for processing NPS and MM to produce various types of liquid and granular nitrogen and phosphorus fertilizers is important.

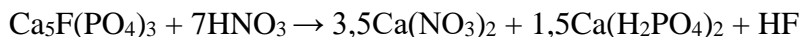
Physico-chemical basis of nitric acid decomposition of phosphate raw materials

The nitric acid decomposition of phosphorites makes it possible to use not only its anion, with which an additional nutrient component is introduced into the fertilizer, but also the chemical energy of the acid.

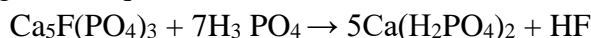
The conditions for the decomposition of phosphates with nitric acid have a significant impact on the composition of the decomposition products and subsequent operations of their processing into fertilizers. Depending on the amount of nitric acid, the process of decomposition of phosphate raw materials can occur with the formation of certain compounds. At a rate of 2 moles of HNO₃ per 1 mole of CaO, calcium nitrate and phosphoric acid are formed in phosphate raw materials:



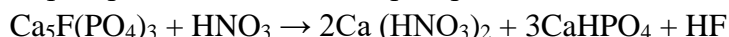
The reaction proceeds at a fairly high speed and the phosphate minerals decompose almost completely. When using a reduced rate of nitric acid (1.4 mol HNO₃ per 1 mol CaO), the process is described by the equation:



In this case, the apatite residue (after decomposition with nitric acid) is decomposed by phosphoric acid according to the equation:

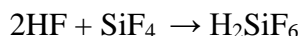
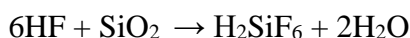
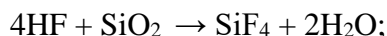


In this case, monocalcium phosphate is released into the solid phase. The reaction proceeds very slowly at a concentration of initial nitric acid of at least 60%. If the process uses 0.8 mol HNO₃ per 1 mol CaO phosphate, then dicalcium phosphate is released into the solid phase.



In this case, the process occurs only when using a very weak acid and high temperature.

Hydrogen fluoride released in the process reacts with silicon dioxide contained in the raw material to form H₂SiF₆ and SiF₄:



Fluorine in the nitric acid extract is mainly in the form of hydrofluorosilicic acid.

The impurities contained in phosphates - calcium and magnesium carbonate, oxides of iron, aluminum and rare earths also interact with nitric acid to form nitrates. Iron and aluminum oxides are also decomposed by the released phosphoric acid to form water-insoluble phosphates (FePO₄, AlPO₄). Therefore, phosphates containing more than 12% Fe₂O₃ (relative to P₂O₅) are considered suitable for chemical processing only after preliminary enrichment.

Characteristics of the materials studied and experimental techniques

To carry out the experiments, unenriched phosphate raw materials (RPR) - phosphate rock of the Central Kyzylkum (CC) - and waste from the enrichment of phosphate rocks of the CC - mineralized mass (MM) from the Kyzylkum phosphate complex were used as starting materials. The chemical compositions of the used phosphorites and mineralized mass are given in Table 1.

Table 1.

Chemical composition of the feedstock.

N	Type of raw material	Chemical composition, mass. %								
		P ₂ O ₅	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CO ₂	SO ₃	F	H.o.
1	NFS	16,97	47,0 2	1,48	1,21	1,28	15,44	1,95	1,92	6,99
2	MM	12,86	36,7 5	8,87	1,17	1,37	15,61	2,00	1,85	11,8 9

We also used unconcentrated 57% nitric acid produced by JSC Maksam-Chirchik according to TSh 6.3-75:2018, and gaseous ammonia according to GOST 6221-90.

Studies on the decomposition of NPS and MM with nitric acid were carried out in a glass reactor equipped with a paddle stirrer and placed in a thermostated container (Fig. 1).

The determination of phosphates was carried out by a differential photometric method based on the formation of a yellow-colored phosphovanadium-molybdenum complex and photometric measurement of the optical density of this complex at a wavelength $\lambda = 430-450$ nm relative to a reference solution containing a known amount of P₂O₅. Phosphate extraction was carried out with a solution of nitric acid.

Methods for performing chemical analyses, determining physical properties and conducting physical and chemical studies

The starting raw materials and the resulting products were analyzed for the content of the following components: nitrogen, calcium, magnesium, aluminum, iron, carbonates, sulfates, insoluble residue, water.

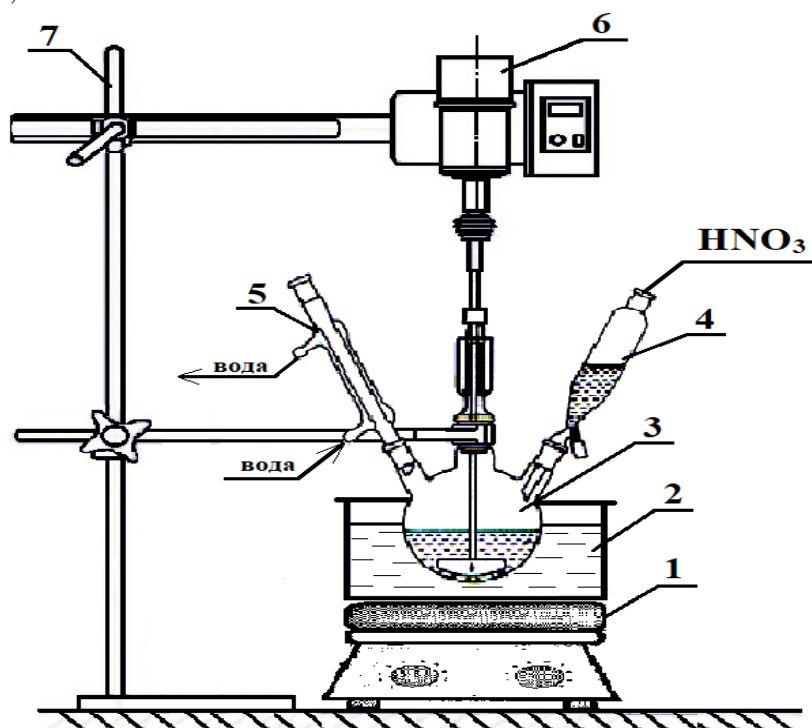


Figure-1. Laboratory setup diagram

1 - electric stove; 2 - water bath; 3 - glass reactor; 4 - long funnel; 5 - reflux refrigerator; 6 - stirrer; 7 - tripod.

Total nitrogen was determined by. The method is based on the reduction of nitrate nitrogen to ammoniacal Devard's alloy, followed by distillation of ammonia and its titrimetric determination.

Ammonium nitrogen was determined by. The method is based on the oxidation of ammonia nitrogen with chloramine to elemental nitrogen in the presence of a phosphate buffer solution with pH 6.7 and potassium bromide; excess chloramine is determined iodometrically.

Nitrate nitrogen was determined by. The method is based on the reduction of nitrate nitrogen with a solution of iron (II) sulfate in an acidic medium in the presence of ammonium molybdate as a catalyst, followed by titration of excess iron (II) sulfate with a solution of potassium permanganate.

Calcium and magnesium were determined by the complexometric method. The method is based on a change in the color of the indicator (fluorexone when determining calcium and acid chromium dark blue when determining magnesium) when calcium and magnesium ions interact with Trilon B.

The content of iron and aluminum was determined by the complexometric method. The method is based on titration of iron with Trilon B in the presence of sulfosalicylic acid as an indicator and back titration of excess Trilon B with a solution of zinc sulfate to determine aluminum in the presence of xylenol orange as an indicator.

Carbon dioxide of carbonates was determined by the accelerated volumetric method. The method is based on the decomposition of carbonates with hydrochloric acid and determining the volume of carbon dioxide released.

Water in solid samples was determined by drying in an oven to constant weight at a temperature of 100-105°C.

The determination of fluorides was carried out by the ionometric method, based on measuring the concentration of fluorine in solution using a fluoride selective electrode without preliminary extraction of fluorine.

To characterize the intermediate and final products, their certain physicochemical properties were studied: density, viscosity, pH, granule strength, friability, moisture capacity, hygroscopic point.

The density of solutions and pulps was determined using a PZh-2 pycnometer. The kinematic viscosity of solutions and pulps was measured with glass capillary viscometers VPZh-1 and VPZh-2.

The pH of solutions and suspensions was determined by the electromechanical method.

To identify the phase composition of starting and intermediate substances and finished products, in addition to chemical analysis, X-ray diffraction, IR spectroscopic, thermogravimetric and scanning electron microscopic, mass spectrometric, and microscopic analysis methods were used.

X-ray diffraction patterns of the samples were taken using a computer-controlled XRD-6100 apparatus (Shimadzu, Japan). In this case, CuK α radiation was used (β -filter, Ni, 1.54178 tube current and voltage mode 30 mA, 30 kV) and a constant detector rotation speed of 4 deg/min with a step of 0.02 deg. ($\omega/2\theta$ -coupling), and the scanning angle varied from 4 to 80°.

The spectra of the samples were recorded on an IRTracer-100 IR-Fourier spectrometer complete with a single-shot ATR attachment with a diamond/ZnSe MIRacle 10 prism. It is designed for the analysis of solid, liquid, paste-like, gel-like and difficult-to-process substances in

the scanning range: 4600 – 600 cm⁻¹. To do this, a sample in powder form was placed on a diamond window in the center of the attachment.

The surface morphology and microstructure study of the samples was carried out using a scanning electron microscope SEM - EVO MA 10 (Carl Zeiss, made in Germany) with an Aztec Energy Advanced X-Act – Oxford Instruments X-ray spectrometer. This device is designed for microscopic analysis of structure and defects, including determination of local elemental composition using energy-dispersive spectroscopy. Experiments on a scanning electron microscope were carried out as follows. To carry out the sample preparation process, a metal alloy holder was installed on the microscope stage, on top of which aluminum foil with a double-sided adhesive surface was glued. The test sample was applied to this foil. Next, the stage was installed in the working chamber of the microscope, from which the air was evacuated to create a vacuum. To carry out the measurement, an accelerating voltage of 12 kV was applied to the filament, while the working distance was 8.5 mm. Images were obtained at scales starting from 50 μm.

Mass spectrometer with inductively coupled plasma ICP-MS iCAP-Qc (Thermo Scientific TM). Designed for determination and quantitative analysis of the elemental composition of various substances. In particular, this device is used to determine trace elements in inorganic and organic materials, and also serves to determine isotopic ratios.

CONCLUSIONS

1. The scientific and technical foundations of the method for producing extraction phosphoric acid by the decomposition of phosphorites and apatite with a mixture of sulfuric and phosphoric acids were further developed.

2. It has been shown that the process of firing the initial phosphorus-containing raw materials significantly affect the patterns of formation of phosphogypsum crystals. A mathematical description of the kinetics of the firing process of phosphate rock has been carried out. It is shown that after effective firing with a decrease in the carbonate part in phosphate raw materials from 11.7% to 3%, with subsequent sulfuric acid decomposition of phosphorites, the size of phosphogypsum crystals increases from 50 to 250 microns.

REFERENCES

1. Hakimov, & B. Haydarov (2023). IMPACT OF REAGENTS-REGULATORS ON FLOTATION. Science and innovation, 2 (A10), 19-22. doi: 10.5281/zenodo.8419901
2. Haydarov, A. Mamirov, & Sh. Pardaboyeva (2023). SYNTHESIS OF NEW MULTIFUNCTIONAL IONITES AND THEIR APPLICATION IN SORPTION OF SOME METALS. Science and innovation, 2 (A7), 156-160. doi: 10.5281/zenodo.8200095
3. Haydarov, G. Ibodullaeva, Sh. Pardaboyeva, & N. Ermamatova (2023). DRINKING WATER PURIFICATION METHODS. Science and innovation, 2 (D5), 178-184. doi: 10.5281/zenodo.7974073
4. Амирова А.М. Физико-химические исследования фосфоритов Центральных Кызылкумов и процессов их кислотной переработки. // Узб. хим. ж.- Ташкент, 1983. - № 1. - С. 18-26.
5. Вольнскова Н.В. Разработка и внедрение технологии производства экстракционной фосфорной кислоты из фосфоритов Центральных Кызылкумов. Дисс. ... канд. техн. наук. - Ташкент, 2010. - 172 с.